CERTIFICATION OF APPROVAL

Physical Solubility of CO_2 in Novel Solvent Called Stonvent Using "N_2O Analogy" Method

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(SITI FATIMAH BINTI HASHIM)

ABSTRACT

Physical solubility of carbon dioxide (CO_2) gas in a novel solvent; Stonvent, has been estimated by applying "Nitrous Oxide (N_2O) Analogy" method and compared to conventional amines in terms of its solubility performance obtained from Henry's law calculations. The analogy is applied due to the reaction between CO_2 gas and Stonvent, will be proven to be valid with spectroscopy test. The experiment was conducted at various temperatures (303.15, 313.15 and 323.15) K with pressure ranges at (10, 45 and 80) bar. A solubility apparatus which consists of two pressure vessels has been used to measure the solubility of N_2O in Stonvent. The experimental Henry's constant of N_2O have been correlated with that of CO_2 in Stonvent. The data obtained demonstrate that the Henry's constant of CO_2 in Stonvent decreases with decreasing temperature and increasing pressure. Lower Henry's constant indicates higher solubility of CO_2 gas in Stonvent. Hence, optimum physical solubility of CO_2 in Stonvent obtained is at 303.15 K and 80 bar. Stonvent also showed a better solubility performance compared to the conventional amines such as monoethanolamine (MEA) due to the lower Henry's constants obtained. Finally, the spectra of Stonvent contacted with N_2O and CO_2 are compared; in which the negligible effect of N_2O vibration showed that the analogy is valid for this experiment.

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ABBREVIATIONS AND NOMENCLATURES

AMP	2-Amino-2-methyl-1-propanol
C_A	Concentration of the absorbed gas
C-O	Carbon – Oxygen bond
CO_2	Carbon dioxide
DEA	Diethanolamine
EC	Equilibrium Cell / Solubility Vessel
H	Henry's constant
H_2S	Hydrogen sulfide
IR	Infrared
K	Kelvin
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MV	Mixing Vessel
n	Number of moles of N_2O gas
N_2	Nitrogen
N_2O	Nitrous oxide
n_{N2O}	N_2O gas introduced to the system or to MV
$n_{N2O(g)}$	Number of moles in the gas phase in EC
$n_{N2O(l)}$	Number of moles of N_2O gas in the liquid phase or the absorbed N_2O gas
P	Absolute pressure
P_1	Initial pressure of MV Initial pressure of EC
P_2	Initial pressure of EC
P_A	Partial pressure of solute above the liquid mixture or Vapour pressure of solute in the mixture
P_{eqm}	Equilibrium pressure
R	Universal gas constant = 0.08314 bar.L/mol.K
T	Absolute temperature
V	Volume of gas
V_a	Air Valve (at the back)
V_b	Vent Valve (at the back)
V_c	N_2 to MV Valve
V_d	N_2O to MV Valve
V_e	Solvent to EC Valve
V_f	MV to EC Valve
V_g	Sample Outlet Valve
V_h	Water Valve
V_i	N_2 to EC Valve
Z	Compressibility factor

CHAPTER 1

INTRODUCTION

1.1 PROJECT BACKGROUND

CO_2, which stands for carbon dioxide is a colourless and odourless gas as well as a natural component of the air. Most of this gas is produced by human beings and respiration of other living things. For instance, exhaled air contains as much as 4% CO_2 or about 100 times the amount of CO_2 inhaled [1]. Meanwhile, the further proportion is produced by the complete combustion of carbon-contained raw materials.

From Figure 1.1 below, CO_2 emission in Malaysia has been reported to be steadily increasing in recent years. Although the number is small relative to the amount of CO_2 emission in Qatar, which is 56.24 tonne per capita [2], efforts to minimize the discharge of the gas should be implemented. Reduction of CO_2 emissions is currently a forefront topic on climate protection. This is due to the fact that CO_2 absorbs part of the heat radiated by the sun, which causes the greenhouse effect and in turn the warming of the earth's atmosphere.

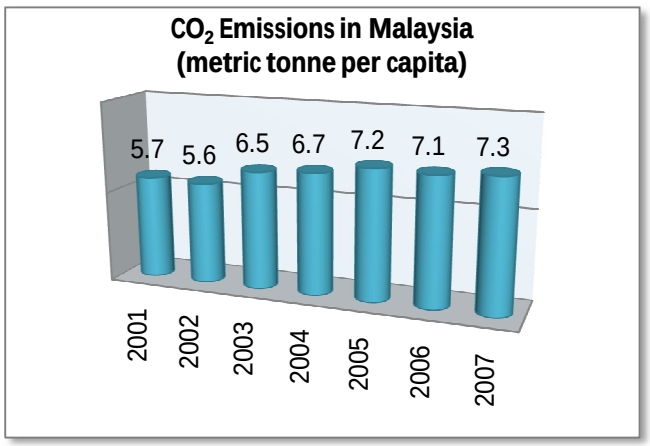

Figure 1.1: CO_2 Emissions in Malaysia [3]

Gas treating or sweetening are both terms used to describe the various processes for removal of certain contaminants; primarily hydrogen sulfide (H_2S) and CO_2, from natural gas or hydrocarbon liquids. The methods of CO_2 removal include chemical absorption with solvent, oxygen/ CO_2 recycle combustion (oxy-fuel), cryogenics processes, adsorption processes such as pressure swing adsorption and thermal swing adsorption; and membrane separation [4]. Among these methods, according to Alie (2004), CO_2 absorption by alkanolamine aqueous solution has been considered as the most efficient way and the most commercial processes for the bulk removal of CO_2 from gaseous streams involve the use of amines [5]. Such streams include natural gases, synthesis gases from gasification of coal and heavy oils, and tail gases from sulphur plants and petroleum chemical plants [6].

Aqueous solutions of amines are widely used in petroleum and natural gas industries in order to remove CO_2, hydrogen sulfide (H_2S) and other contaminants present in the natural gas streams. Currently, many researches have been conducted with the focus of amine treating for the treatment of natural or refinery gases. Amine gas sweetening is a proven technology that removes CO_2 and H_2S from natural gas and liquid hydrocarbon streams through absorption and chemical reaction.

Each amine that is presently being the spotlight offers distinct advantages to specific treating problems. The widely used primary amine is the monoethanolamine (MEA) as it is the cheapest one among all the amines; which is used in low pressure natural gas treatment applications that require stringent outlet gas specifications. Meanwhile, the secondary amine like diethanolamine (DEA) is used in medium to high pressure treating that does not require reclaiming. As for the tertiary amine like methyldiethanolamine (MDEA) has a higher affinity for H_2S than CO_2 which allows some CO_2 'slip' while retaining H_2S removal capabilities. Finally, there are some formulated or specialty solvents which consist of a variety of blended solvents that improve the efficiency of CO_2 removal [7].

In this project, the physical solubility of CO_2 in a novel solvent is studied using the "N_2O Analogy" method at (303.15, 313.15 and 323.15) K and (10, 45 and 80) bar, temperature and pressure, respectively. The novel solvent is called Stonvent, which is a formulated amine. The theories of the project will be explained in Chapter 2.

1.2 PROBLEM STATEMENT

CO_2 is the key greenhouse gas that causes climate change and global warming due to human activities. As estimated by The International Energy Agency, the world energy consumption would increase by 70% between 2000 and 2030. The anthropogenic CO_2 emissions should rise from its current rate of 28 billion tons to 38 billion tons in 2030. Without actions aiming at limiting CO_2 emissions, the concentration of this greenhouse gas in the atmosphere could double near 2100 [8].

Worldwide major source of this harmful gas emission is the combustion of fossil fuels such as coal, oil and gas in power plants, industrial facilities and other sources [2]. Large quantities of CO_2 are produced by lime kilns as well as ammonia and hydrogen production from natural gas or other hydrocarbon raw materials [1]. Meanwhile, Figure 1.2 shows the major sources of CO_2 emission in Malaysia in percentages. As part of the major contributor to the greenhouse gas emission to the atmosphere, oil and gas industry shall find options to minimize the emission of the gas from its operational activities.

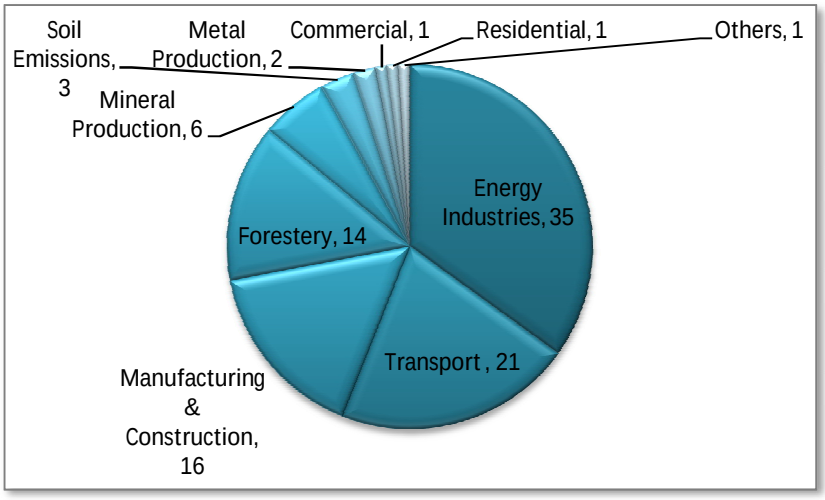

Figure 1.2: Major Sources of CO_2 Emission in Malaysia (%) [3]

Apart from the recognition of greenhouse gas, CO_2, which is termed as “acid gas”, forms carbonic acid when combined with water. This is corrosive to the equipment which can increase the operation costs. When CO_2 is present, the most common forms of corrosion (Figure 1.3) include uniform corrosion, pitting corrosion, wormhole attack and etc. Hence, this requires CO_2 to be removed. In addition, CO_2

removal is often required in order control the heating value or the fuel quality of the natural gas.

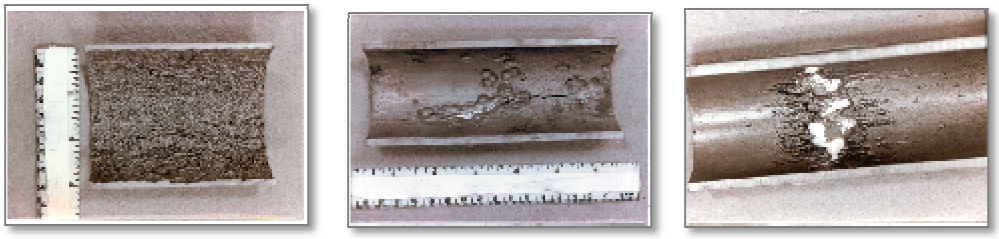

Figure 1.3: (left) Uniform Corrosion (Middle) Pitting Corrosion (Right) Wormhole [9]

Amines have been used for many years to remove acid gases from natural gas and there is many existing technical information on their performance capabilities. Amine gas sweetening process is based on the reaction of a weak base (alkanolamine) and a weak acid (CO_2) to produce a water-soluble amine acid gas salt. This reaction that creates the weak amine-sulfide salt is reversible at elevated temperatures, which allows the amine to be regenerated and recycled to the contactor for additional acid gas removal [10]. For instance, the reaction for diethanolamine is shown below:

$$\underset{\text{DEA}}{HOC_2H_4NH_2} + \underset{\substack{\text{Hydrogen}\\\text{Sulfide}}}{H_2S} = \underset{\substack{\text{DEA-Sulfide}\\\text{Salt}}}{HOC_2H_4NH_3^+HS^-}$$

However, the regeneration step requires a large amount of energy. The heat duty requirement in the stripper is the sum of three heat duties:

- The heat duty required for preheating the solvent before the stripper
- The heat duty required for reversing the reaction between CO_2 and the amine; to break the chemical bonds between the absorbed CO_2 and solvent
- The heat duty required for generation of the steam within the amine regenerator to strip the CO_2 from the solvent [11].

Thus, the development of new solvents aiming towards limiting the global energy consumption is now has become a necessity. In addition, from the view of the environmental aspects, CO_2 gas is released to the atmosphere during the regeneration step.

Therefore, with the new formulated amine; Stonvent, used in this project, these problems could be minimized or even eliminated. This study is useful for future

researchers who are interested to further investigate the characteristics of Stonvent in CO_2 removal and gas sweetening processes. Furthermore, in-depth study on solubility and other characteristics of Stonvent can contribute in designing gas-treating operators such as the industrial absorber.

1.3 OBJECTIVE AND SCOPE OF STUDY

The objective of this study is to estimate the physical solubility of CO_2 in a new solvent called Stonvent using the "N_2O Analogy" method. The physical solubility refers to the portion of the total carbon dioxide that is not reacted, thus it is determined in terms of Henry's constant. Meanwhile the analogy is applied since CO_2 reacts with the solvent solution, thus its physical solubility cannot be measured directly. However, in this project, the molecular properties of the novel solvent shall not be enclosed due to its confidentiality in a department project.

The experimental data for the solubility of N_2O gas in Stonvent is taken at temperatures and pressures ranging at (303.15, 313.15 and 323.15) K and (10, 45 and 80) bar, respectively. The physical solubility of N_2O gas in Stonvent is determined as a function of concentration of the N_2O gas absorbed in the solvent. From the data obtained in the experiments, Henry's constant of CO_2 in Stonvent is determined using the following correlation:

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} \qquad (1.1)$$

Performance of CO_2 in Stonvent is compared to conventional amines such as monoethanolamine (MEA). This is achieved by comparing the Henry's constant of CO_2 in both Stonvent and MEA under the same parameters; in which lower Henry's constant indicates higher solubility.

Sample of each run is tested with Raman spectroscopy test to compare the variation in the spectrum of pure Stonvent and the spectrum of Stonvent contacted with N_2O and CO_2 gas. This test is also meant to prove that the "N_2O Analogy" method is valid to be used in estimating the Henry's constant of CO_2 in Stonvent.

CHAPTER 2

LITERATURE REVIEW

2.1 SOLUBILITY OF GAS

Solubility is simply defined as the ability of a substance to dissolve. In a process of dissolving, the substance which is being dissolved is called the solute while the substance in which the solute is dissolved is called the solvent [12]. In this project, the solute is N_2O gas whereas water and Stonvent act as the solvent.

Solubility of a gas in a liquid depends on the temperature, partial pressure of the gas over the liquid as well as nature of the solvent and the gas. Gas solubility is always limited to the equilibrium between the gas and the saturated solution of the gas. The dissolved gas will always follow Henry's law [13].

The concentration of the dissolved gas depends on the partial pressure of the gas. The partial pressure controls the number of gas molecule collisions with the surface of the solution. If the partial pressure is doubled, the number of collisions with the surface wall will also double. Increased number of collisions would produce more dissolved gas. The illustration of the phenomena is shown in Figure 2.1 below.

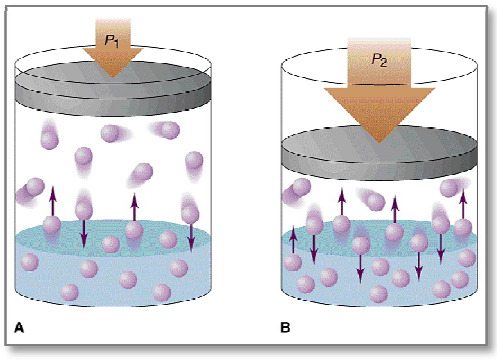

Figure 2.1: Solubility of a Gas Depends on Its Partial Pressure above the Solution [13]

The number of gas molecules leaving the gas phase to enter the solution equals to the number of gas molecules leaving the solution. If the temperature remains constant, increasing the pressure will increase the amount of dissolved gas.

2.1.1 "N_2O Analogy" Method

Physical solubility data of CO_2 gas is required to predict the gas absorption rate. However, physical solubility of CO_2 gas in aqueous amine solutions cannot be measured directly due to the chemical reaction undergone by CO_2 gas with these solvents. The measurement of physical solubility is based on determining the concentration of gas absorbed in a solvent at equilibrium. Thus, when the absorbed gas reacts with the solvent, the physical equilibrium cannot be measured.

Clarke (1964) initially proposed the use of a similar gas which is nonreactive in the test solution to measure the solubility. A proportionality constant is later used when calculating the solubility of CO_2. He assumed that the ratios of the solubility of CO_2 and N_2O in water to that in aqueous solutions of organic solvents is similar within 5% or better at the same temperature. In other words, the ratios of $\frac{H_{CO_2}}{H_{N_2O}}$ in water and in solutions having different amine concentrations are assumed to be constant at constant temperature [14].

According to Park and Sandall (2001), due to the similarities between N_2O and CO_2 with regard to its molecular configuration, electronic structure, molar volume and molecular weight, one usually practises the "N_2O Analogy" method [15].

Haimour and Sandall (1984) also proved that the predictions of physical solubility using the "N_2O Analogy" method can be applied to predict the absorption rate of CO_2 gas in aqueous MDEA; under the conditions of very short contact times where the chemical reaction does not affect the absorption rates [16]. They expressed the analogy, at 25°C, in the following form:

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{Solution} = \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = 0.73.$$

In addition, it is reported that Laddha et al (1981) investigated the solubility of CO_2 and N_2O in aqueous solutions of organic compounds that do not react with respect to both solutes and organic alcohols which have quite similar structure to MEA and DEA [17]. In this work, they concluded that the ratio of solubilities remained constant at 1.37 at 25°C for those solutions and "N_2O Analogy" may be applied to determine the solubility of CO_2 gas in aqueous alkanolamine solutions.

Al-Ghawas et al (1989) also reported that the "N_2O Analogy" method can also be used to estimate the solubility of COS in aqueous MDEA [18].

This method was later used by many researchers such as Weiland and Trass (1971) [19], Saha et al (1993) [20], Browing and Weiland (1994) [21] as well as Ko and Li (2000) [22] to estimate solubility of CO_2 gas in many amine solvents. Thus, the "N_2O Analogy" method is proven to be a valid method to estimate the physical solubility of CO_2 gas in amine solvents.

As explained in Chapter 1.3, the spectroscopy test of the samples obtained from the experiments will be analyzed in order to approve of the validity of the analogy.

2.1.2 Henry's Law

Besides mole fraction at a standard pressure and the Ostwald coefficient, Battino and Clever (1966) stated that Henry's law constant can also be used as a measure of gas solubility [23]. Besides, Saylor *et al* also concluded that Henry's law is applicable in aqueous solutions of slightly soluble organic liquids [24].

In an ideal solution of two liquids, both components obey Raoult's law. Nevertheless, for real solutions at low concentrations, although the solvent (the major component of the solution) usually obeys Raoult's law, the solute (the minor component of the solution) does not [24].

Henry's law can be applied to relate the equilibrium concentration of the gas in the liquid as a function of its partial pressure in the gas phase. In Henry's law (Equation 2.1), it is basically stated that the vapour pressure of the solute is proportional to the

mole fraction of a slightly soluble gas dissolved in a liquid; in which the constant of proportionality is not the vapour pressure of the pure substance.

$$p_A = C_A H_A \qquad (2.1)$$

Where, p_A = Partial pressure of solute above the liquid mixture or Vapour pressure of solute in the mixture

C_A = Concentration of the absorbed gas

H_A = Henry's constant of the solute

*A to distinguish solute from solvent (B)

As mentioned above, a mixture in which the solute obeys Henry's law while the solvent obeys Raoult's law; the mixture is called an ideal-solute solution [4]. This phenomenon occurs at low concentrations since the solvent is in large excess, thus its molecules are likely to be surrounded by other solvent molecules. Their environment is very much like that of the pure liquid, hence the similarity of behaviour of pure liquid. On the other hand, the solute exists in low concentration, thus more likely to be surrounded by solvent molecules. Therefore, their environment is quite different from in the pure solute and consequently their behaviour is greatly modified.

However, exceptions arise when the solute and solvent are of very similar structure. In this case, although the solute molecules are surrounded by solvent molecules, their environment is not dissimilar to that in pure solute, their behaviour will not be greatly altered and both mixtures tend to obey Raoult's law [25].

N_2O obeys Henry's law well due to its low solubility in alkanolamine solutions. Some substances such as sulphur dioxide do not obey Henry's law, even at low pressures due to the effect of ionization [21].

2.2 BLENDED AMINE, STONVENT AS SOLVENT

Due to the confidentiality of the components in Stonvent, the components of the solvent shall not be enclosed. Nevertheless, Stonvent is a modified blended amine, which possesses the advantage of producing product in solid form. The solid product will not require any treatment prior to discharge. Thus, the emission of greenhouse

gas to the atmosphere can be minimized. Today, there are many available papers on the better performance of blended amine than single amine as solvent in acid gas sweetening.

Chakravarty (1985) first suggested the use of aqueous blends of primary and tertiary amines for stripping CO_2 [26]. Shen and Li (1992) measured the CO_2 solubility in aqueous blends of MDEA and MEA at the total amine concentration of 30 wt% [27]. Jou et al (1994) determined the CO_2 solubility in four aqueous mixtures of MDEA with MEA at temperatures of 25 to 120 °C over pressure ranging from 0.001 to 19930 kPa [28]. Xu et al (1998) measured the solubility of CO_2 in 4.28 kmol/m^3 MDEA with piperazine, which concentrations ranging from 0 to 0.515 kmol/m^3 and CO_2 partial pressures from 3.83 to 76.77 kPa [29]. Kierzkowska-Pawlak and Zarzycki (2002) also investigated the solubility of CO_2 and N_2O in single MDEA and blend of ethanol and MDEA [30]. Last but not least, blended amines are also being studied in simulations of the process using software i.e. Aliabadi et al (2009) simulated the use of amine mixtures consisting of MDEA, MEA and DEA using HYSYS [31]. All of the authors noticed the significant enhancement of CO_2 absorption rate when a small quantity of a reactive amine is added.

The objective of the solvents blends is to activate an aqueous solution of tertiary amine, hindered amine or potassium carbonate by a primary or secondary amine [11]. MDEA, a tertiary amine, contains three non-hydrogen groups attached to the nitrogen atom. A tertiary amine can react only indirectly with CO_2 through a base-catalyzed reaction. This reaction is relatively slow compared to the reaction between a primary or secondary amine with CO_2. As for primary or secondary amines, CO_2 can react directly and carbamates are formed. However, the fast carbamate formation reaction leads to significantly higher amounts of energy requirement in regeneration of each mole of CO_2.

Therefore, as the higher CO_2 reaction rates of the primary and secondary amine is combined with the higher CO_2 loading capacity of the tertiary amine results in substantial lower solvent circulation rates compared to MDEA alone [31]. A lower circulation rate leads to a reduced regeneration energy requirement and a reduced of the pumping energy cost. However, Polasek et al (1990) reported that when mixtures of amines are used for bulk CO_2 removal, the performance of the unit is often very

sensitive to one or more of the operating parameters [32]. Hence, a good parametric analysis of the operating parameters should be performed in each case.

2.3 SPECTROSCOPY TEST

Spectroscopy is a study of how species such as atoms, molecules and solutions react to light [33]. The electromagnetic radiation absorbed, emitted or scattered by the species is analyzed. As for Raman, it depends on the molecule's vibrations when reacted to light. A beam of radiation such as laser is normally passed through a sample and the radiation exiting the sample is measured.

The "Raman Effect" was discovered by an Indian scientist, Dr. Chandrasekhara Venkata Raman together with K.S. Krishnan; enabling him to win the Nobel Prize in Physics in 1930 [34]. He noticed that the visible wavelength of a small fraction of the radiation scattered by certain molecules differs from that of the incident beam. He also observed that the change in frequency depends on the chemical structure of the molecules responsible for the scattering.

When light hits a sample, the molecules in the sample is excited and forced to vibrate and move, thus reaching a higher level of energy and is brought back down. These vibrations are measured to study the reaction of the molecules to light. In Raman spectroscopy, the frequency of radiation is varied, producing a spectrum which shows the intensity of the exiting radiation for each frequency. This spectrum also shows which frequencies of radiation have been absorbed by the molecules to raise it to higher vibrational energy states.

The frequency of the scattering light can be these two of the following [35]:

- At the original frequency (Rayleigh scattering)
  Radiation scattering to the lower frequency side of the Rayleigh line is called Stokes scattering while to the higher frequency side of the Rayleigh line is called anti-Stokes scattering.
- At some shifted frequency (Raman scattering / shift)
  Can correspond to rotational, vibrational or electronic frequencies.

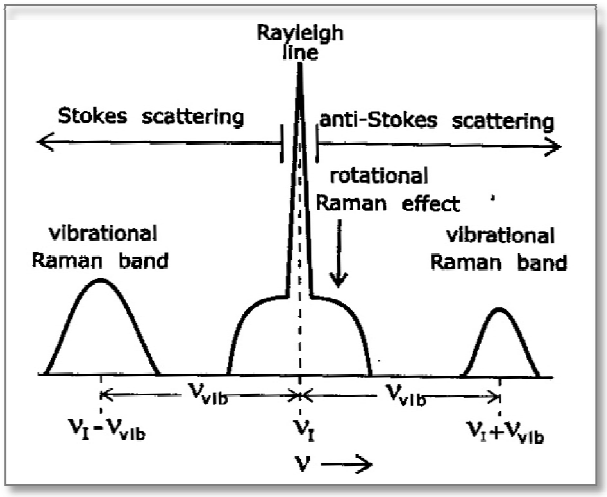

Figure 2.2: Schematic Diagram of a Raman Spectrum [35]

Basically, Raman spectroscopy is complementary to Infrared (IR) spectroscopy in that both can be used as tools to characterize the molecular vibrations. However, in the case of Raman, the sampling is more convenient since glass containers may be used and solids do not have to be mulled or pressed into discs. In addition, in Raman spectroscopy, spectral measurements on vibrations made in the visible region-glass cells may be used while IR spectroscopy only allows halide optics; which are expensive, fragile and water soluble, to be used. Besides, Raman spectroscopy is more widely used since the advent of Ft-Raman systems and remote optical fibre sampling. Earlier difficulties with laser safety, stability and precision have been overcome. Figure 2.3 summarizes some of the differences between the two techniques.

	Raman	Infrared
Ease of sample preparation	Very simple	Variable
Liquids	Very simple	Very simple
Powders	Very simple	Simple
Polymers	Very simple*	Simple
Gases	Simple	Very simple
Fingerprinting	Excellent	Excellent
Best vibrations	Symmetric	Asymmetric
Group Frequencies	Excellent	Excellent
Aqueous solutions	Very good	Very difficult
Quantitative analysis	Good	Good
Low frequency modes	Excellent	Difficult

* True for FT-Raman at 1064 nm excitation.

Figure 2.3: Differences between Raman and IR [36]

Other than these characteristic of Raman and IR, following are some other characteristics [35]:

- Raman experiment uses a laser beam of a very small diameter (1-2mm). Therefore, a very small quantity of the sample is required to be analyzed.
- Selection rules are significantly different. Some vibrations are only Raman active, some are only IR active and some are both.
- Some vibrations are inherently weak in IR and strong in Raman spectra.
- As water is a very weak Raman scatterer, Raman spectra of samples in aqueous solution and hygroscopic air sensitive compounds can be obtained without major interference from water vibrations and its rotation fine structures that are extremely strong in IR absorption spectra.
- Sample container in Raman technique is made from glass. In IR technique, glass is impossible to be used since it absorbs IR radiation.
- Raman spectra tend to be less cluttered with peaks than IR spectra (Figure 2.4). Hence, peak overlap in mixtures is less likely and quantitative measurements are possibly simpler.

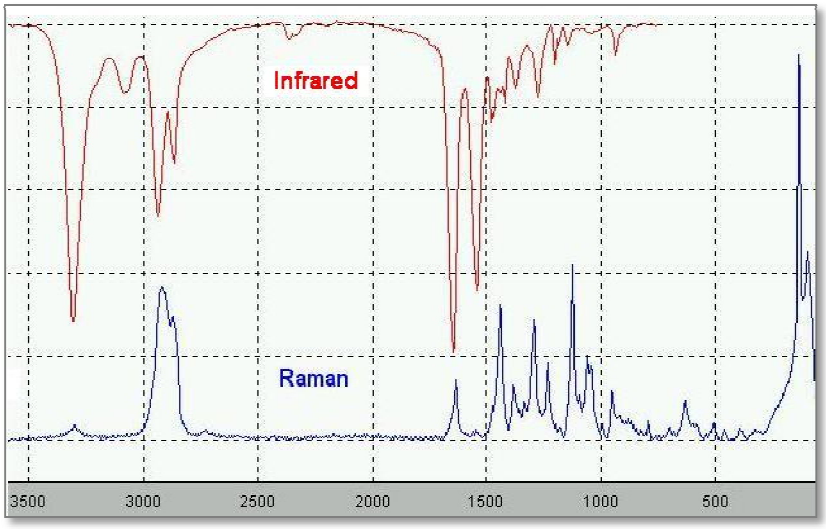

Figure 2.4: Infrared and Raman Spectra of Polyamide (Nylon 66) [37]

There are two different approaches used for the interpretation of vibrational spectroscopy and explanation of molecular structure, which are:

- Use of group theory with mathematical calculations of the forms and frequencies of the molecular vibrations,
- Use of empirical characteristic frequencies for chemical functional groups.

Generally, many identification problems are solved using the empirical approach. Certain functional groups show characteristic vibrations in which only the atoms in that particular groups are displaced. Figure 2.5 displays the vibrational frequency for common functional groups.

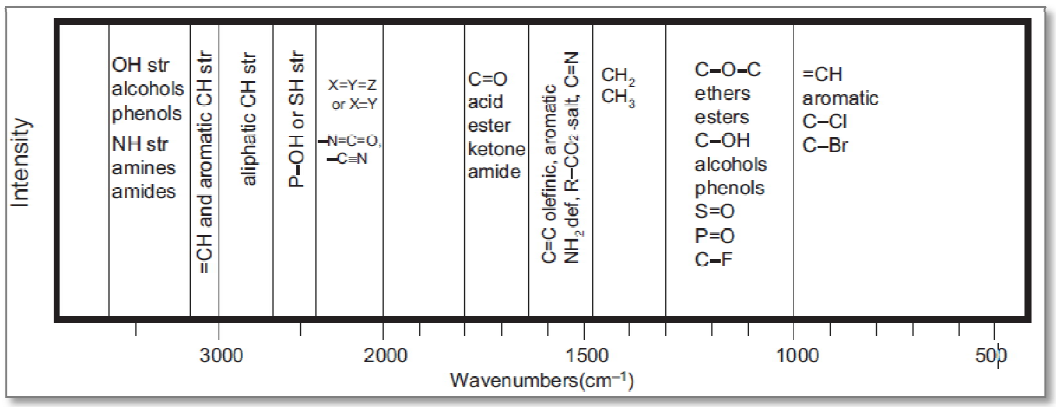

Figure 2.5: Vibrational Frequency for Common Functional Groups [36]

There are many studies done on solubility of CO_2 by analyzing the Raman spectroscopy of the gas contacted with a variety of solvents. For instance, Cabaco et al (2011) studied the Raman spectroscopy after the introduction of CO_2 in 1-Butyl-3-methyl-imidazolium-trifluoro acetate ionic liquid to assess the nature of the interaction between their molecules [38]. Meanwhile, Mysen and Virgo (1980) also analyzed the Raman spectrum to determine the structural role of CO_2 in silicate melts [39].

CHAPTER 3

METHODOLOGY

3.1 MATERIALS AND EQUIPMENTS

The materials involved in this experiment are listed as the following:

i. Nitrus oxide, N_2O gas
ii. Nitrogen, N_2 gas
iii. Formulated amine, Stonvent
iv. Distilled water
v. Acetone

The equipments used for this experiment are as listed below:

i. Two (2) pressure cells; mixing vessel and equilibrium cell
ii. Compressor
iii. Magnetic stirrer
iv. Metering pump
v. Water bath

The tools used for this experiment are as listed below:

i. Dropper
ii. Syringe
iii. Sample bottles

In compliance to the safety requirements of the laboratory regulations, the following are worn throughout the experiments:

i. Lab coat
ii. Covered shoes
iii. Gloves
vi. Safety goggles

3.2 RESEARCH METHODOLOGY

In order to achieve the objectives, the study is conducted based on the flowchart (Figure 3.1) below. The research is divided into four parts, namely; literature review, solubility experiment, Raman spectroscopy test and data analysis.

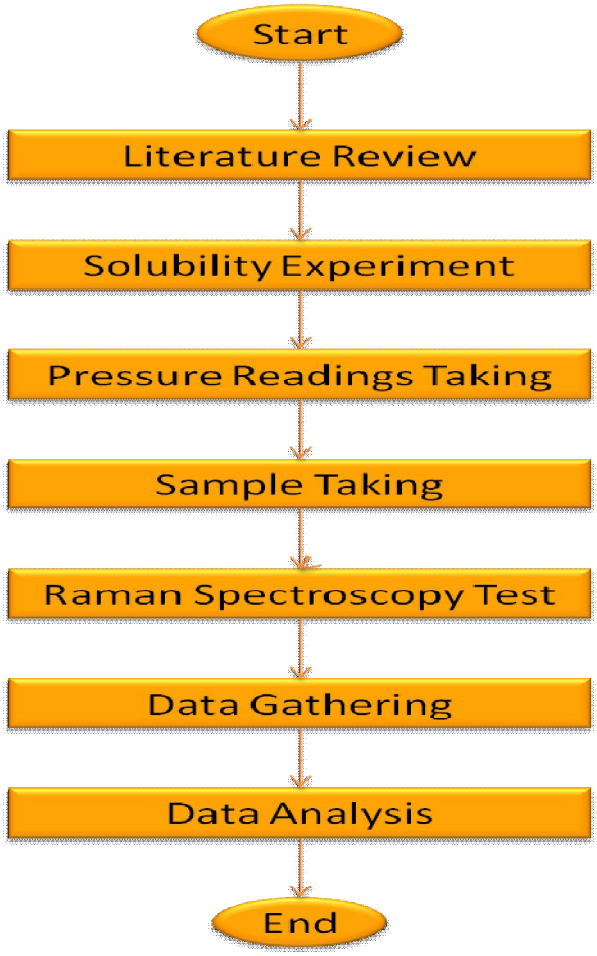

Figure 3.1: Research Flowchart

3.2.1 Solubility Experiment

Two pressure vessels are mainly used in this experiment in which one is the mixing vessel (MV); to store the N_2O gas, and another one is the equilibrium cell (EC); where the gas and solvent is mixed. Both of the vessels are thermo regulated with water bath set at the required temperatures. In order to elevate the pressure, a

compressor is used. After the parameters are set, the basic experiment procedures (Figure 3.2), pressure reading takings and sample takings are repeated for temperatures and pressures ranging at (303.15, 313.15 and 323.15) K and (10, 45 and 80) bar, respectively. The Stonvent is obtained straight from the manufacturer, thus the concentration cannot be manipulated. Meanwhile, the experiment for determining the Henry's constant of N_2O gas in water is conducted under a constant pressure of 10 bar and various temperatures of (303.15, 313.15 and 323.15) K with the use of distilled water. The constant pressure parameter is chosen since pressure only has slight effect on the solubility of gas in water.

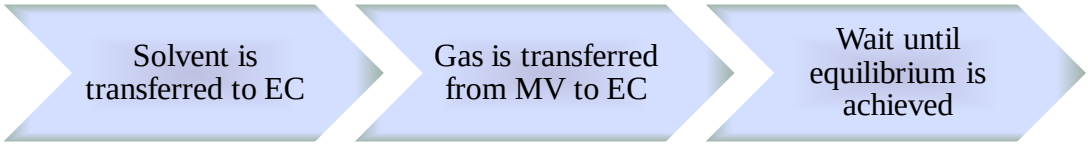

Figure 3.2: Basic procedures

The following pressure readings are taken for data analysis:

i. P_1, the initial pressure of MV
ii. P_2, the stabilized pressure of MV and EC when gas is transferred
iii. P_{eqm}, the equilibrium pressure of EC

Figure 3.3 shows the solubility apparatus used while the schematic diagram of the experimental setup to determine the physical solubility of CO_2 using the "N_2O Analogy" method is shown in Figure 3.4.

Figure 3.3: Solubility Apparatus

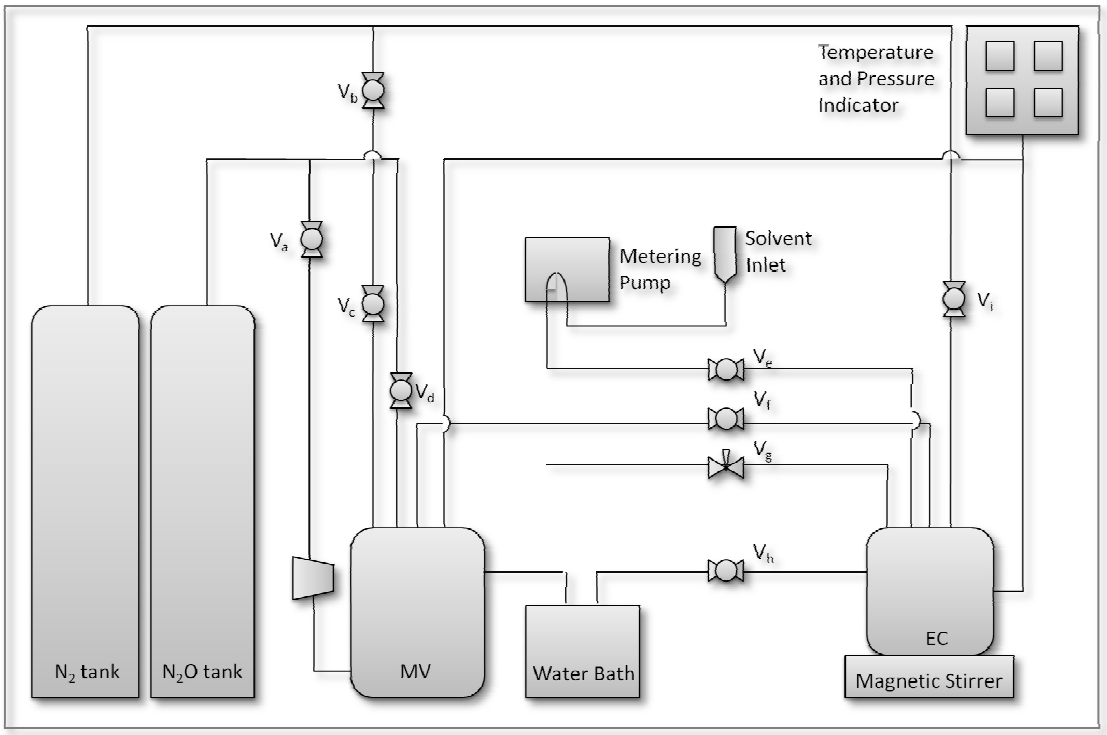

Figure 3.4: Schematic Diagram of the Experimental Setup

Where, MV : Mixing Vessel

EC : Equilibrium Cell / Solubility Vessel

V_a : Air Valve (at the back)

V_b : Vent Valve (at the back)

V_c : N_2 to MV Valve

V_d : N_2O to MV Valve

V_e : Solvent to EC Valve

V_f : MV to EC Valve

V_g : Sample Outlet Valve

V_h : Water Valve

V_i : N_2 to EC Valve

The following procedure is the detailed procedure conducted in the Unit Operation Lab of Chemical Engineering Department located at 03-00-06. They are repeated for each run except for A (Start Up) and H (Shut Down) which are carried out to start and end every session.

A. Start Up

i. The main power sources on the computer, temperature and pressure indicator, metering pump and water bath are switched on.

ii. The gas cylinders of N_2 and N_2O are opened.

B. EC Purging (*and MV after start-up)

i. V_i is opened to let N_2 gas flow to EC.

ii. At the computer, go to 'Flow Control' > 'Channel 1' the flow rate of N_2 gas is set to be in between 0-10 L/min.

* During start up, V_c and V_f are opened to purge MV with N_2 gas.

iii. V_g is opened to let the gas flows out.

iv. The flow of N_2 gas at 'Channel 1' is set to be 0 L/min after a few minutes.

v. V_i and V_g are closed.

* V_c and V_f are closed.

C. Temperature Setting

i. V_h is opened to let water flows into EC.

ii. The desired temperature for EC is set.

D. MV Pressurizing

i. V_d is opened to let N_2O gas flow into it.

ii. The flow rate of N_2O gas in 'Channel 4' is set to be in between 0-6 L/min.

iii. V_a is opened to start pumping the gas into MV. Pressure increase will be observed on the pressure indicator.

iv. When the desired pressure is reached, V_a is closed.

v. The flow rate of N_2O in 'Channel 4' is set to be 0 L/min.

vi. V_d is closed.

E. Solvent transfer

i. 5 mL of solvent is put in the Solvent Inlet.

ii. V_e is opened. Make sure all other valves are closed.

iii. The blue button on the Metering Pump is pressed to let the solvent flows into EC.

iv. When all the solvent is transferred, the blue button is pressed to stop the flow and V_e is closed.

v. When the pressure stabilizes, pressure reading of MV is taken as the initial pressure, P_1.

F. Gas Transfer from MV to EC

i. At the computer, go to 'Data Logging' and log is started.

ii. V_f is opened to transfer the N_2O gas to EC.

iii. When the pressure of both MV and EC is approximately similar to each other, close V_f is closed.

iv. The reading of the second pressure, P_2 of MV is taken.

v. The magnetic stirrer is turned on.

vi. When there is no or very little change in pressure in EC, the equilibrium is achieved. The equilibrium pressure of EC, P_{eqm} is taken.

G. Sampling

i. The magnetic stirrer is turned off.

ii. The EC is purged with N_2 gas by opening V_b and V_i to bring down the pressure to atmospheric pressure to avoid spilling.

iii. When the pressure is achieved, V_b and V_i are closed.

iv. V_g is opened carefully to avoid damage to the valve.

v. The sample is poured into a sample bottle and kept for spectroscopy test.

H. Shut Down

i. EC is washed with acetone. Instructions in Part E are followed.

ii. At the computer, 'Exit' and Yes' is clicked to exit the software.

iii. Computer is shut off.

iv. The power sources on the computer, temperature and pressure indicator, metering pump and water bath are switched off.

v. V_h is closed to avoid water from spilling out from the water bath.

3.2.2 Raman Spectroscopy Test

Raman spectrum is taken for the samples collected before and after N_2O is introduced to Stonvent. These spectra are compared to Stonvent contacted with CO_2. The equipment used is shown in Figure 3.5 below. The laser is set to 10 MW power and 50 µm aperture slit. Basically, the test is run by aligning each sample (Figure 3.6) to the laser beam on the equipment in order to allow the laser to pass through the sample. The spectrum will then be shown on the software.

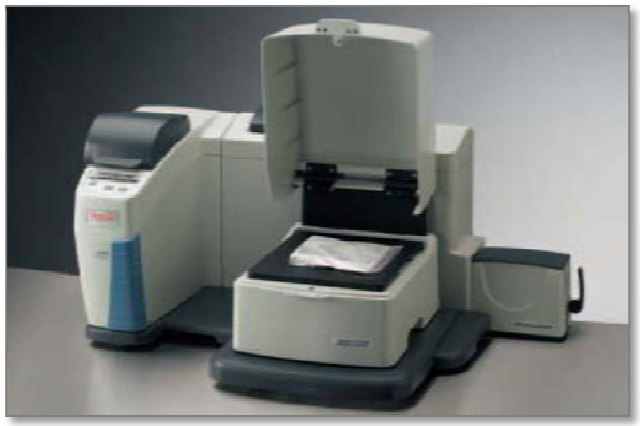

Figure 3.5: Raman Setup

Figure 3.6: Sample Bottles

The detailed procedure of conducting this test is as follow:

i. Samples are filtered to avoid contamination.
ii. Sample is put on the equipment.
iii. Lid is closed to avoid light from entering the equipment. This is to allow sole presence of the laser light to hit the sample.
iv. The test is started by clicking 'Start' in the software.
v. Step (ii) to Step (iv) is repeated for all samples.
vi. The broadband trend of the pure solvent and solvent with N_2O gas contact is evaluated and compared to those contacted with CO_2 gas.

3.2.3 Data Analysis

3.2.3.1 Henry's Constant of N_2O and CO_2 in Solvent Determination

The amount of N_2O gas can be determined by applying the Ideal Gas Law equation (Equation 3.1). It relates pressure, temperature and volume of the ideal or perfect gas which can be a good approximation to the behaviour of the gas.

$$PV = nRT \qquad (3.1)$$

Where, P = Absolute pressure = Gauge pressure + Atmospheric pressure
V = Volume of gas
n = Number of moles of N_2O gas

R = Universal gas constant = 0.08314 bar.L/mol.K

T = Absolute temperature

However, the Ideal Gas Law is only accurate at relatively low pressures and high temperatures. It also does not apply to all gases under all conditions [40]. Hence, in order to consider for the deviation from the ideal condition, another factor is included. It is called the Gas Compressibility Factor, Z, which is obtained from the compressibility factor chart (Appendix A). This correction factor is dependent on the pressure and temperature for each gas being considered, as some gases are not ideal even at atmospheric pressure and ambient temperature. If Z is equal to unity, the gas is perfectly ideal whereas for real gases, Z can be either lower or higher than 1. Thus, Equation 3.1 becomes the True Gas Law or the Non-Ideal Gas Law, which is as follow:

$$PV = ZnRT \tag{3.2}$$

The volume of the MV and the EC is 3 L and 50 mL, respectively. However, EC is changed to a 100 mL vessel due to maintenance operation.

Using the pressure difference of the initial pressure of MV (P_1) to the initial pressure of EC (P_2), the moles of N_2O gas introduced to the system or to MV can be calculated.

$$\Delta P = P_1 - P_2 \tag{3.3}$$

$$n_{N_2O} = \frac{\Delta P \, V_{MV}}{Z \, R \, T} \tag{3.4}$$

The number of moles in the gas phase in EC can be calculated using the equilibrium pressure, P_{eqm}. Equation 3.5 displays the formula.

$$n^{g}_{N_2O} = \frac{P_{eqm} \, (V_{EC} - V_{Stonvent})}{Z \, R \, T} \tag{3.5}$$

From Equation 3.4 and 3.5, the number of moles of N_2O gas in the liquid phase or the absorbed N_2O gas can be determined. The equation is as follows:

$$n^{l}_{N_2O} = n_{N_2O} - n^{g}_{N_2O} \tag{3.6}$$

From the number of moles of N_2O absorbed, the concentration of the absorbed N_2O gas by Stonvent, C_{N2O} is calculated using Equation 3.7 below:

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}} \qquad (3.7)$$

Henry's law states that partial pressure of the gas is proportional to the concentration of the gas absorbed by the solvent, i.e.

$$p = CH \qquad (3.8)$$

From Equation 3.8 above, the Henry's constant, H can be determined for N_2O gas.

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}} \qquad (3.9)$$

The Henry's constant for N_2O in water is obtained from the experiment following the above calculations, replacing the subscript 'Stonvent' to 'Water'.

Using Equation 1.1 in Chapter 1, the "N_2O Analogy" method correlation is used to estimate the CO_2 solubility in Stonvent. The data for the Henry's constant of CO_2 gas in water is obtained from literature.

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} \qquad (1.1)$$

Where, H = Henry's constant

After the Henry's constant for CO_2 is obtained for all temperatures and pressures, the graph of H_{CO2} versus 1000/T for each temperature and pressure are plotted. The lower the Henry's constant is, the higher solubility of CO_2 in solvent.

The experiment at atmospheric pressure is conducted differently as the pressure is low enough that does not require two pressure vessels to transfer the gas. The mole of N_2O is calculated directly from the pressure difference of the initial pressure and the equilibrium pressure.

$$n^l_{N_2O} = \frac{\Delta P\ (V_{EC} - V_{Stonvent})}{Z\ R\ T} \qquad (3.10)$$

The proceeding calculations are similar to Equation 3.6 to Equation 1.1.

3.2.3.2 Spectroscopy Test

The spectrum of the pure Stonvent is compared to the spectrum of Stonvent with contact of N_2O and CO_2. The effect of N_2O and CO_2 contact to the spectra are analyzed by referring to the functional group vibrational frequency in Figure 2.5. Significant effect indicates that the gas reacts with the solvent. Therefore, in this case, insignificant effect of N_2O contact to the spectra will prove that the N_2O does not react with Stonvent, hence, validating that the "N_2O Analogy" method is applicable for this experiment.

3.2.3.3 Data Comparison

The results of the experiments are compared with that of conventional amines in order to calibrate them with the established data. However, most of the journals are conducted under atmospheric pressure and to strengthen the comparison between this study and conventional amines, the study is extended to conducting experiments at:

- Atmospheric pressure for solubility of CO_2 in Stonvent, and
- High pressures (10 and 45) bar for solubility of one of the conventional amine, MEA. 80 bar pressure cannot be conducted due to the limited time.

3.3 KEY MILESTONES

With the assistance and guidance by the Final Year Project Committee, the key milestones (Figure 3.7) of this project could be conducted on time.

Activity	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
Literature Review								Mid Semester Break								
Solubility Experiment																
Submission of Progress Report																
Spectroscopy Test																
Pre-EDX																
Submission of Draft Report																
Submission of Dissertation (Soft Bound)																
Submission of Technical Paper																
Oral Presentation																
Submission of Project Dissertation (Hard Bound)																

Figure 3.7: Gannt Chart

CHAPTER 4

RESULTS AND DISCUSSION

4.1 HENRY'S CONSTANT OF N_2O AND CO_2 IN SOLVENT

In this experiment, the physical solubility of N_2O gas in the novel solvent, Stonvent, is determined at temperatures ranging at (303.15, 313.15 and 323.15) K and pressures of (10, 45 and 80) bar. Meanwhile, as mentioned in the previous chapter, the experiment for determining the Henry's constant of N_2O in water is done under constant pressure of 10 bar.

Referring to Equation 1.1 shown in Chapter 1 and the previous chapter, in order to determine the Henry's constant of CO_2 gas in Stonvent using the "N_2O Analogy" method, the data for Henry's constant of N_2O and CO_2 gas in water are also required. Henry's constant for N_2O gas in water is obtained experimentally while the latter is taken from Al-Ghawas et al. (1989) [18], which is shown in Table 4.1 below.

Table 4.1: Henry's Constant of CO_2 in Water [18]

T (K)	H (kPa.m^3/kmol)
303.15	3394.388
313.15	4249.571
323.15	5166.562

From the experiment, the pressure difference before and after the mixing of gas and solvent are taken. At temperature of 303.15 K and 10 bar, the calculations to determine the Henry's constant of CO_2 in Stonvent are done as follow:

A. Henry's Constant for N_2O in Water at 303.15 K and 10 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{10\ bar}{72.7\ bar}$$
$$= 0.1376$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{303.15\ K}{310.15\ K}$$
$$= 0.9774$$

From the compressibility factor chart in Figure A.1,

Z = 0.95

$$\Delta P = P_1 - P_2$$
$$= 10.07 - 9.92$$
$$= 0.15 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\ V_{MV}}{Z\ R\ T}$$
$$= \frac{(0.15)(3)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0188 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\ (V_{EC} - V_{Water})}{Z\ R\ T}$$
$$= \frac{(9.39)\ (0.05-0.005)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0176 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0188 - 0.0176$$
$$= 0.0011 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$

$= \frac{0.0011}{0.005}$

$= 0.2293$ mol/L

$$\left(H_{N_2O}\right)_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$

$= \frac{9.39}{0.2293}$

$= 40.9549$ bar.L/mol

$= 4095.4850$ kPa.m^3/kmol

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4095.485} = 0.8288$$

A. Henry's Constant for N_2O in Stonvent at 303.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.95.

$\Delta P = P_1 - P_2$

$= 11.20 - 10.79$

$= 0.41$ bar

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$

$= \frac{(0.41)(3)}{(0.95)(0.08314)(303.15)}$

$= 0.0514$ mol

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$

$= \frac{(7.43)\,(0.05-0.005)}{(0.95)(0.08314)(303.15)}$

$= 0.0140$ mol

$$n^{l}_{N_2O} = n_{N_2O} - n^{g}_{N_2O}$$

$$= 0.0514 - 0.0140$$

$$= 0.0374 \text{ mol}$$

$$C_{N_2O} = \frac{n^{l}_{N_2O}}{V_{Stonvent}}$$

$$= \frac{0.0374}{0.005}$$

$$= 7.4809 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$

$$= \frac{7.43}{7.4809}$$

$$= 0.9932 \text{ bar.L/mol}$$

$$= 99.3191 \text{ kPa.m}^3\text{/kmol}$$

B. Henry's Constant for CO_2 in Stonvent at 303.15 K and 10 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$

$$= (99.3191)\ (0.8288)$$

$$= 82.3168 \text{ kPa.m}^3\text{/kmol}$$

Based on the calculations on the obtained data; in which the detailed calculation is shown in Appendix A, Table 4.2 shows the Henry's constants of N_2O in water and Stonvent as well as the Henry's constants of CO_2 in Stonvent. From the data, the graph of H_{N2O} in water versus 1000/T (Figure 4.1) is plotted.

Table 4.2: Henry's Constant of N_2O in Water and Stonvent, and CO_2 in Stonvent*

T (K)	$H_{N2O/H2O}$	10 bar		45 bar		80 bar	
		H_{N2O}	H_{CO2}	H_{N2O}	H_{CO2}	H_{N2O}	H_{CO2}
303.15	0.829	99.319	82.317	84.834	70.312	53.573	44.402
313.15	0.815	183.047	149.162	142.217	115.890	84.024	68.470
323.15	0.899	245.081	220.331	178.757	160.705	132.948	119.522

*Henry's constants are in $kPa.m^3/kmol$

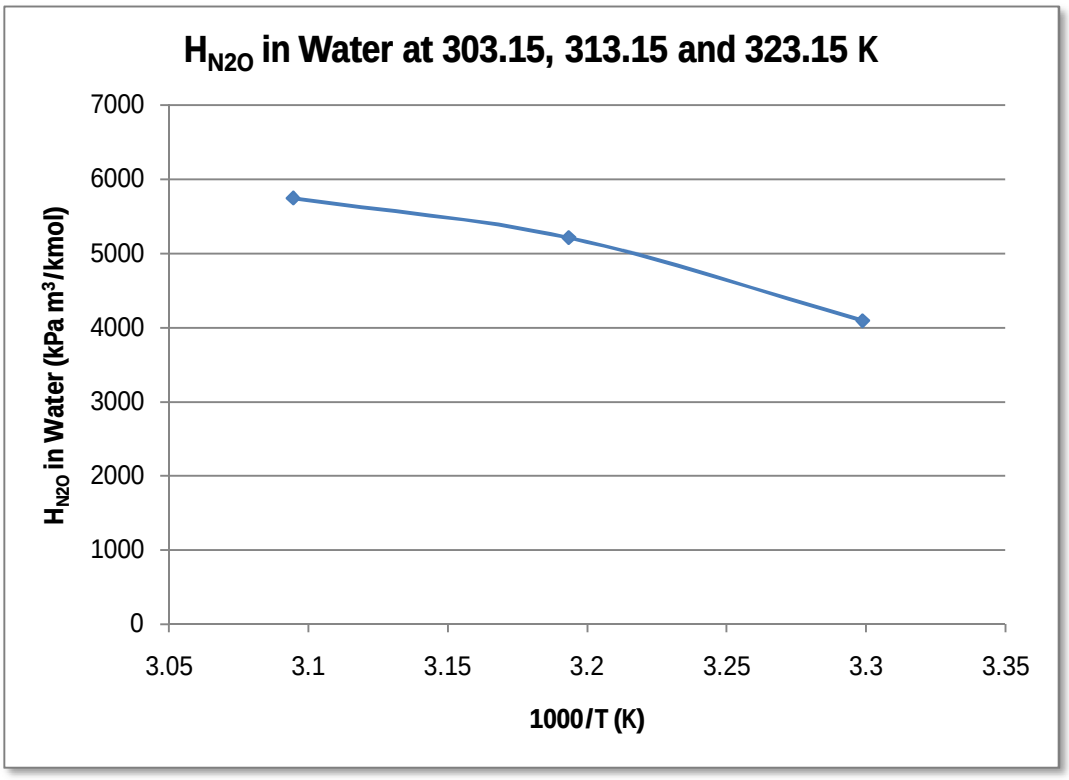

Figure 4.1: H_{N2O} in Water

Based on Figure 4.1, the trend of H_{N2O} in water declines as temperature decreases. As mentioned earlier, lower Henry's constant indicates higher solubility; thus, N_2O is absorbed more at 303.15 K compared to the higher temperatures; 313.15 and 323.15 K. Solubility of N_2O in water is determined in order to calibrate the data with data found in literatures which will be explained later.

Figure 4.2 shows the plot of Henry's constant of CO_2 in Stonvent at different temperatures and pressures.

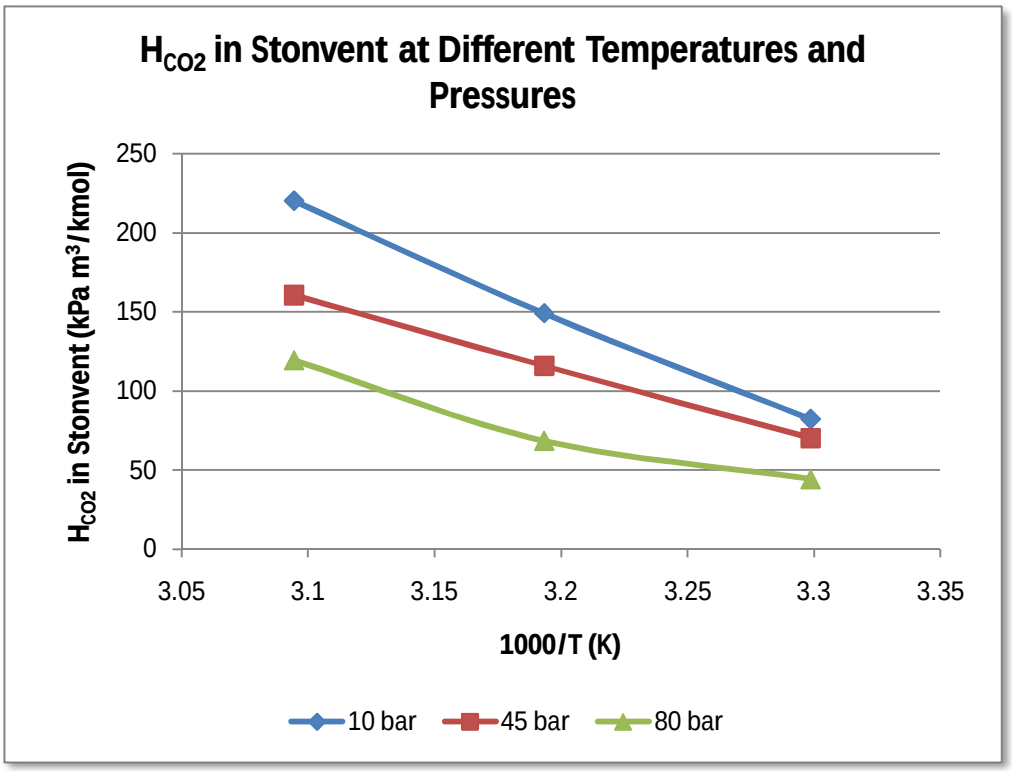

Figure 4.2: H_{CO2} in Stonvent at Different Temperatures of (303.15, 313.15 & 323.15) K and Pressures of (10, 45 & 80) bar

Similar to the trend of Henry's constant of N_2O in water, CO_2 in Stonvent also shows the same decline as the temperature decreases. Thus, higher solubility of CO_2 in Stonvent is achieved at lower temperature. The reason of this occurrence is as the temperature starts rising, the molecules in the liquid expands, thus dissolution of the gas molecules is more favoured.

On the other hand, Henry's constants decrease as the pressure is increased. Therefore, higher absorption of CO_2 in Stonvent is attained at higher pressure. This is because partial pressure of the gas controls the number of collisions between the gas molecule and the surface of the solution, consequently more dissolved gas is obtained as the pressure is increased since the number of collisions increases.

From the analysis, the optimum condition for solubility of CO_2 in Stonvent under high pressure condition is at the lowest temperature; 303.15 K, and highest pressure; 80 bar.

4.2 SOLUBILITY COMPARISON

Due to the limitation of papers of amine done under high pressures, this study is extended to conducting the experiment at atmospheric pressure condition. Therefore, with the results obtained, the solubility cell can be calibrated with N_2O absorption in water. Table 4.3 shows the data obtained for the experiment conducted under atmospheric pressure condition.

Table 4.3: Henry's Constants Obtained at Atmospheric Pressure

T (K)	$H_{N2O/H2O}$ (kPa.m^3/kmol)	$H_{N2O/St}$ (kPa.m^3/kmol)	$H_{CO2/St}$ (kPa.m^3/kmol)
303.15	4259.795	2975.223	2370.785
313.15	5173.427	4229.73	3474.396
323.15	6279.836	5226.53	4299.983

Figure 4.3 shows the comparison between the Henry's constant of N_2O in water obtained from this study and those of which obtained from literature [18], [41], [42] and [43]. From the comparison between this study and the literature, the results obtained from this study are in agreement with the literature data. The trend obtained is similar to what achieved by other researchers, which is Henry's constant declines with decreasing temperature.

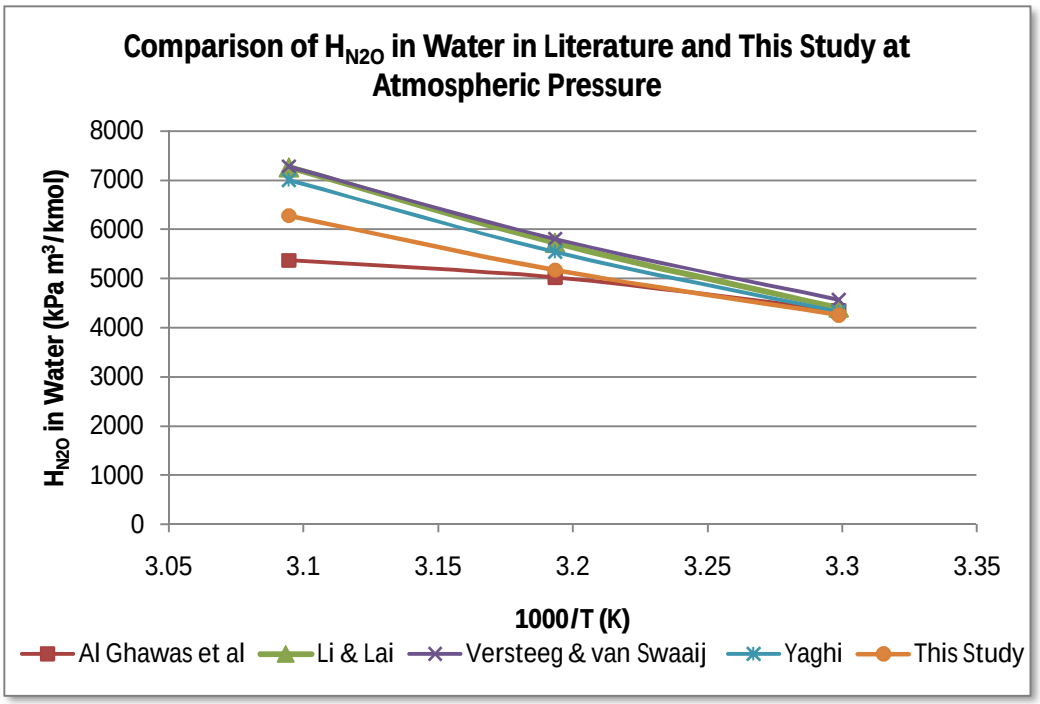

Figure 4.3: Comparison of Henry's Constant of N_2O in Water at Atmospheric Pressure [18], [41], [42], [43]

Meanwhile, Figure 4.4 shows another comparison of Henry's constant of CO_2 in Stonvent with conventional amines; MEA, MDEA and 2-Amino-2-methyl-1-propanol (AMP); each is at 30 mass % concentrations [41], at atmospheric pressure. As the Henry's constant for Stonvent is much lower than all of the single amines, the solubility performance of Stonvent is much better than the conventional amines. Therefore, Stonvent proves to be a better solvent for CO_2 removal.

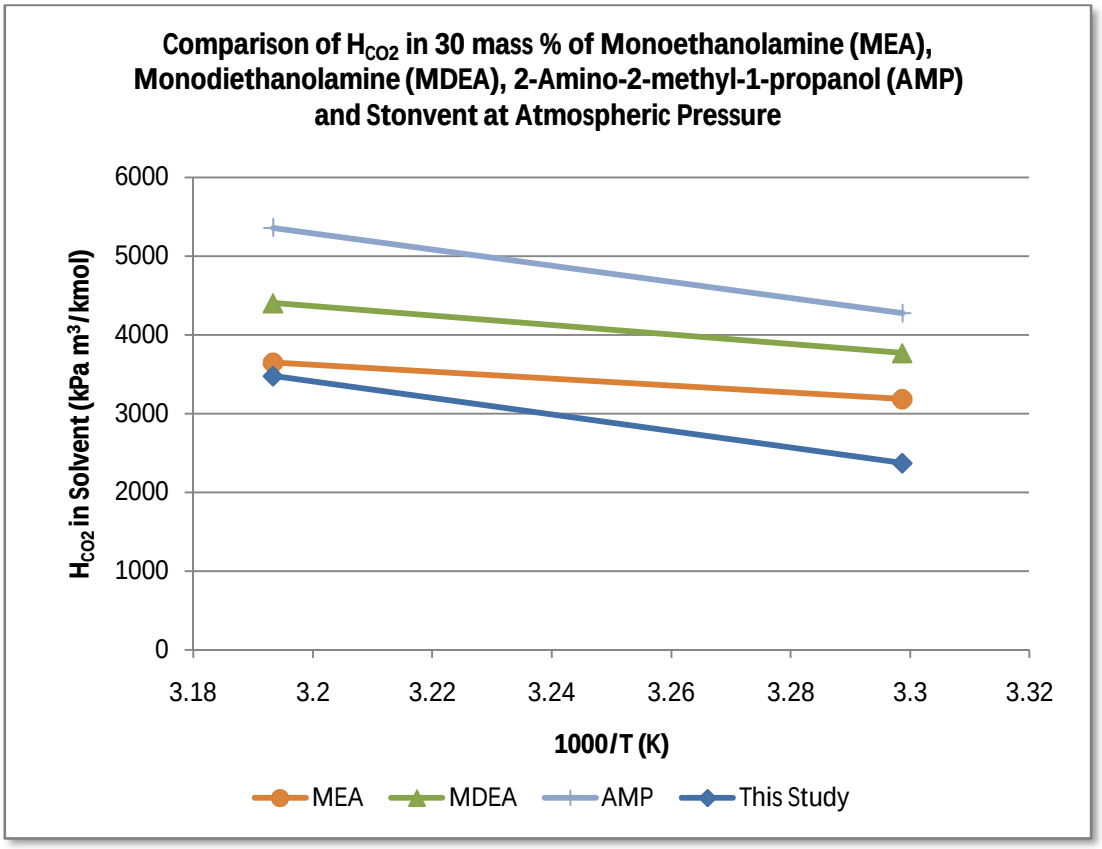

Figure 4.4: Comparison of Henry's Constant of CO_2 in Stonvent and Single Amines (30 mass % MEA, MDEA & AMP) [41] at Atmospheric Pressure

Since Stonvent is a new formulated amine, or in another word; the new blend of amines, a comparison of Henry's constant of CO_2 in Stonvent is made to that of the blended conventional amines [41], which are the blends of MEA and MDEA as well as blends of MEA and AMP. Again, the plots show Henry's constant of CO_2 in Stonvent is much lower than the conventional amines, proving that Stonvent acts as a better solvent for CO_2 removal.

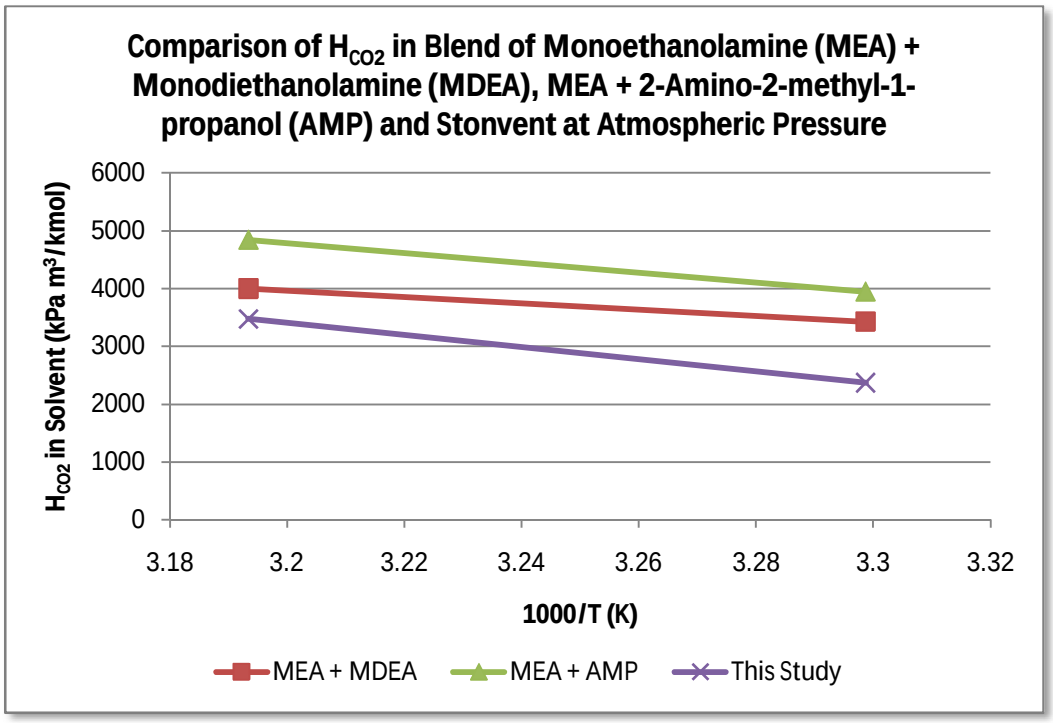

Figure 4.5: Comparison of Henry's Constant of CO_2 in Stonvent and Blended Amines (MEA and MDEA & MEA and AMP) [41] at Atmospheric Pressure

As mentioned earlier, this study is extended to conducting the experiment with MEA at high pressures of (10 and 45) bar in order to get a better comparison of its Henry's constants with that of Stonvent's. Table 4.4 shows the data obtained for Henry's constants of CO_2 in MEA at 10 and 45 bar.

Table 4.4: Henry's Constants of CO_2 in MEA

T (K)	10 bar		45 bar	
	H_{N2O}	H_{CO2}	H_{N2O}	H_{CO2}
303.15	471.906	391.121	357.649	296.424
313.15	766.073	624.260	670.431	546.324
323.15	904.317	812.994	868.298	780.612

Figure 4.6 and Figure 4.7 display the comparison of the Henry's constants of CO_2 obtained for Stonvent and MEA at 10 and 45 bar, respectively. Even at high pressures, Stonvent absorbs more CO_2 than MEA since its Henry's constants are much lower at each pressure.

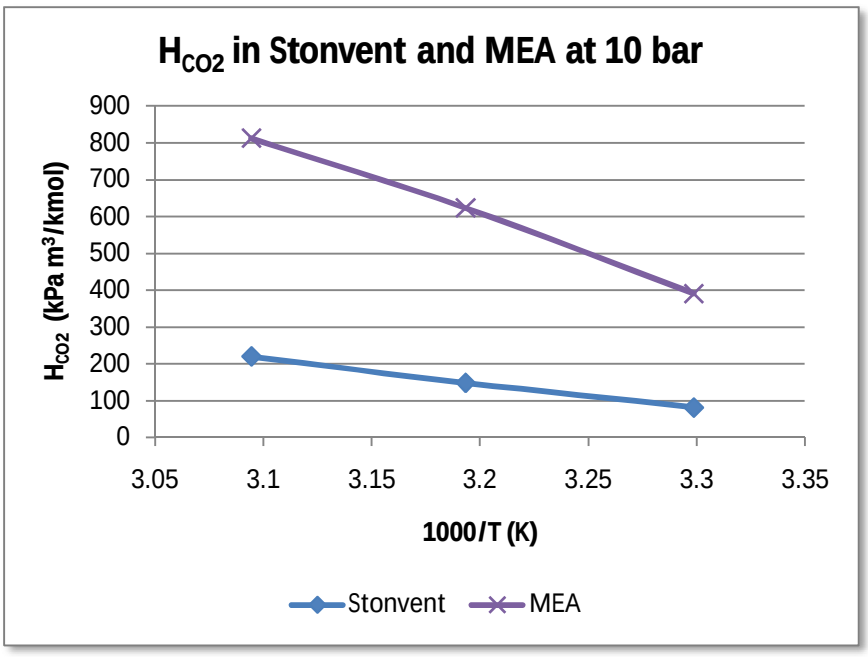

Figure 4.6: Henry's Constants of CO_2 in Stonvent and MEA at 10 bar

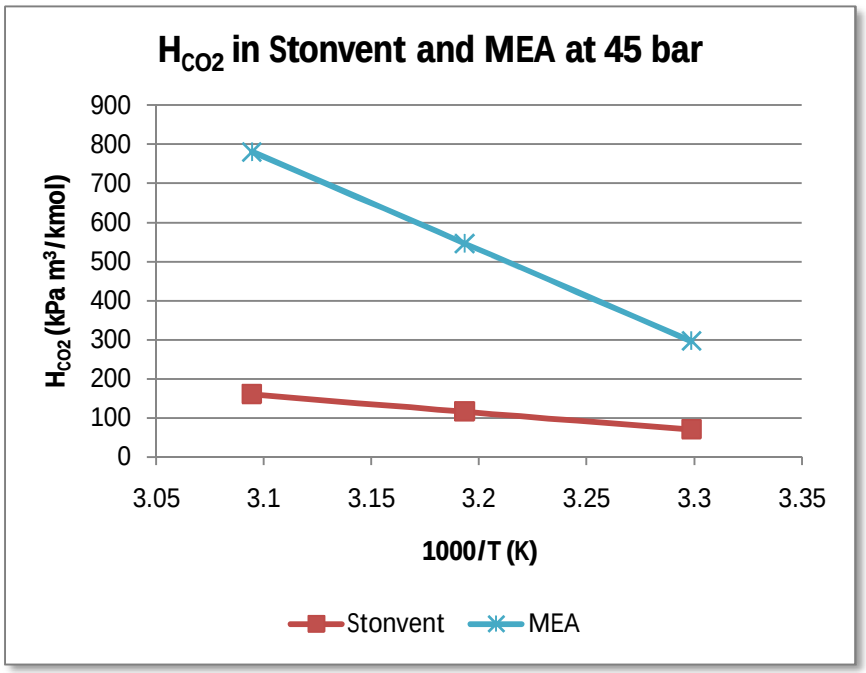

Figure 4.7: Henry's Constants of CO_2 in Stonvent and MEA at 45 bar

Regardless on the solvent, state of the solvent; whether it is single or blended, or the condition of the experiment conducted, Stonvent produces a much lower Henry's constant in all of the comparisons. As lower Henry's constant indicates higher solubility, Stonvent is proven to be a much better solvent in CO_2 removal than the conventional amines being compared to.

4.3 SPECTROSCOPY TEST

The spectroscopy test is conducted in order to demonstrate that the "N_2O Analogy" method is valid for this experiment. With Raman spectroscopy test, spectrum of the pure Stonvent (Figure 4.8) can be compared to the spectrum of Stonvent with contact of N_2O (Figure 4.9) and CO_2 (Figure 4.10), which was taken at 10 bar and 313.15 K condition. Meanwhile, Figure 4.11 displays the overlay of the three spectra for better view.

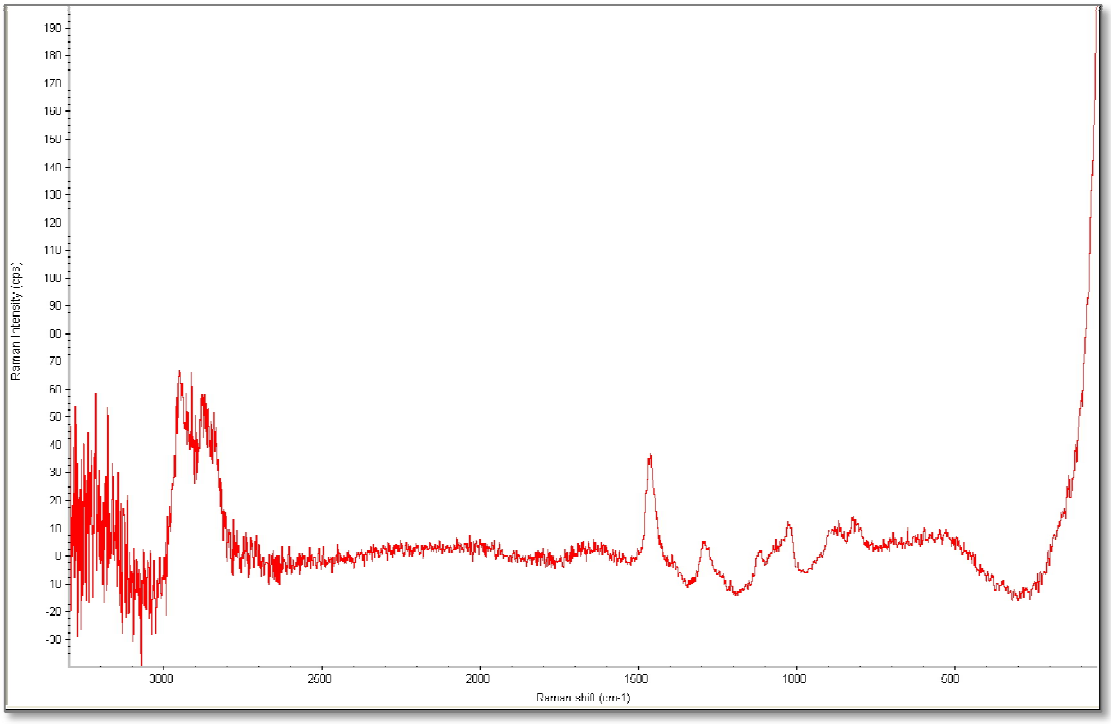

Figure 4.8: Spectrum of Pure Stonvent

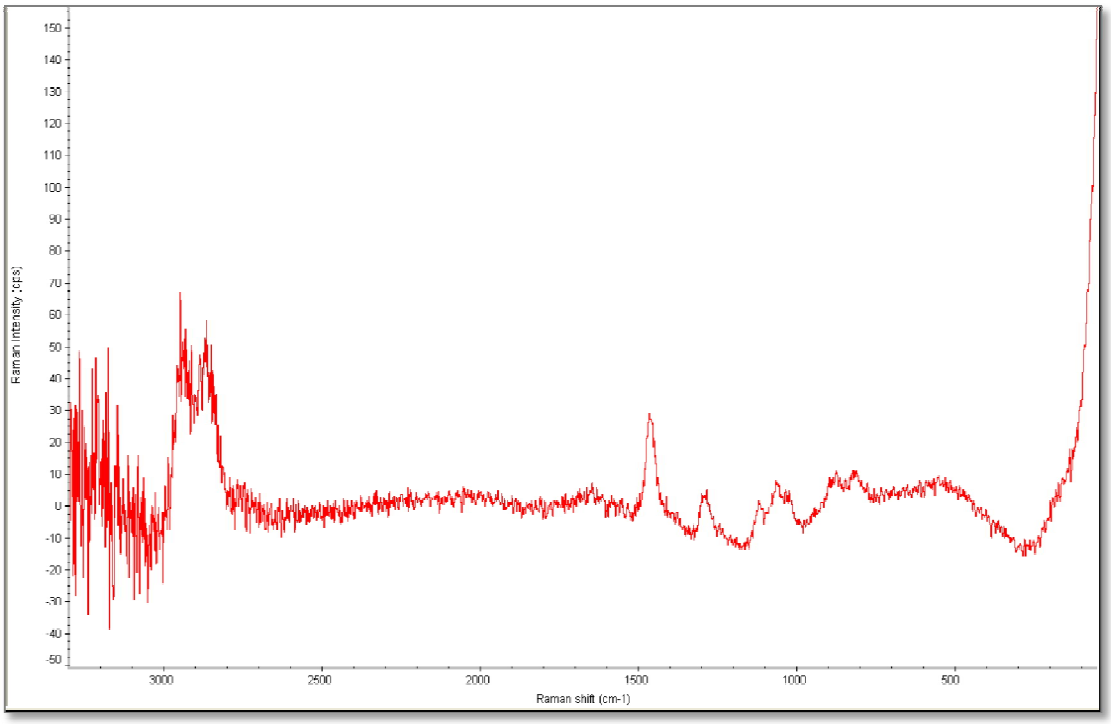

Figure 4.9: Spectrum of Stonvent with N_2O Contact

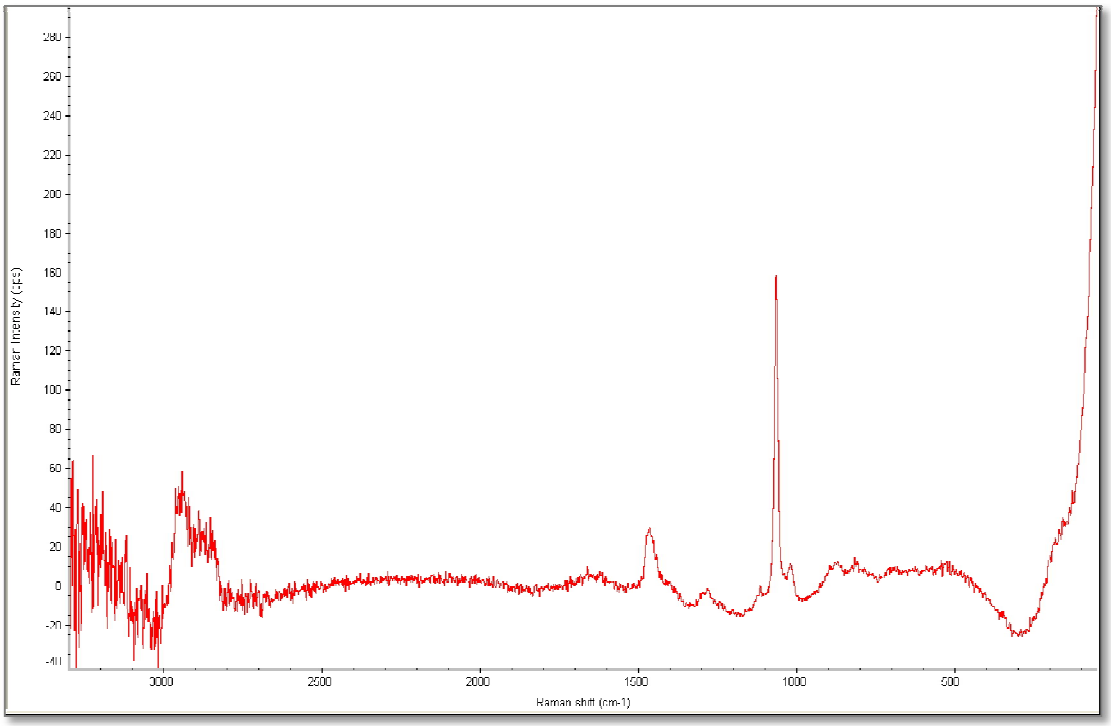

Figure 4.10: Spectrum of Stonvent with CO_2 Contact

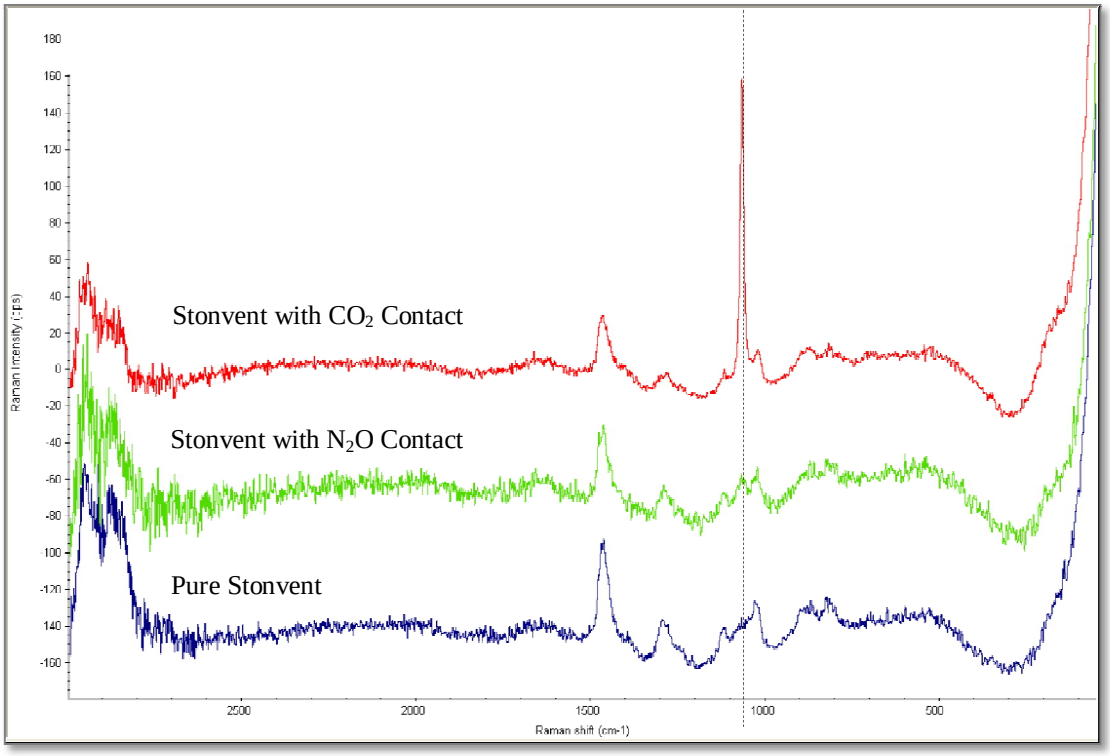

Figure 4.11: Spectra of Pure Stonvent, Stonvent with N_2O Contact and Stonvent with CO_2 Contact

Based on Figure 4.10, the variation or effect of the CO_2 contact can be viewed clearly when comparing the three spectra together. Referring to Figure 2.5 in Chapter 2, at Raman shift of 1080 cm-1, the effect of CO_2 contact is significant as the Raman spectroscopy detects the presence of C-O bond; which indicates that Stonvent has reacted with CO_2. Meanwhile, there is no significant effect on the vibration at the same Raman shift in Stonvent contacted with N_2O. Therefore, it is clear that the "N_2O Analogy" method is valid for this experiment.

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

In this investigation, the Henry's constant of CO_2 in the new solvent called Stonvent has been estimated using the "N_2O Analogy" method over a wide temperature and pressure range, (303.15, 313.15 and 323.15) K and (10, 45 and 80) bar, respectively. Due to the fact that solubility of gas increases with decreasing Henry's constant, the lowest Henry's constant at which the optimum condition for physical solubility of CO_2 in Stonvent for this study is achieved at the lowest temperature, 303.15 K, and highest pressure, 80 bar. Therefore, Stonvent would be a suitable solvent in the industrial CO_2 removal operations.

Based on the comparison made with conventional amines, Stonvent produced lower Henry's constant, which indicates higher solubility of CO_2, making it a better solvent than conventional amines such as MEA.

From the Raman spectroscopy test, "N_2O Analogy" method is accepted for this study. The effect of N_2O in the spectrum is found to be insignificant, thus negligible, compared to the significant effect of CO_2. The negligible effect shows that N_2O does not react with Stonvent during absorption.

In-depth study on the characteristics of Stonvent should be performed by any researchers. In future work, the solubility measurement for Stonvent can be conducted at higher pressure up to 150 bar since most industrial operations are done under high pressure condition. In addition, the measurement can be conducted using different concentrations of Stonvent. Finally, the characteristics of Stonvent can be studied in removal of other gases such as hydrogen sulphide as the solubility data are important in designing the industrial operations.

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APPENDIX A

Volume of Mixing Vessel (MV) = 3.000 L
Volume of Equilibrium Cell (EC) = 0.050 L
New Volume of Equilibrium Cell = 0.100 L *
Volume of Stonvent = 0.005 L
Universal Gas Constant = 0.083144 bar.L/mol.K
Critical Pressure of N_2O = 72.7 bar
Critical Temperature of N_2O = 310.15 K
*Use this volume for equilibrium cell as it was changed to a new one.
(For experiments at 303.15 K, 80 bar and 323.15 K, 45 bar)

$$P_r = \frac{P}{P_c}$$
$$T_r = \frac{T}{T_c}$$

Gas Compressibility Factor, Z is obtained from Figure A.1.

1. Calculation for High Pressure Experiments

From the basis of Gas Law (Equation A.1), the moles of the absorbed gas can be determined.

$$PV = ZnRT \qquad (A.1)$$

Using the pressure difference of the initial pressure of MV (P_1) to the initial pressure of EC (P_2), the moles of N_2O gas introduced to the system or to MV can be calculated.

$$\Delta P = P_1 - P_2 \qquad (A.2)$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T} \qquad (A.3)$$

The number of moles in the gas phase in EC can be calculated using the equilibrium pressure, P_{eqm}.

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T} \qquad (A.4)$$

Number of moles of N_2O gas in the liquid phase or the absorbed N_2O gas can be determined.

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O} \qquad (A.5)$$

From the number of moles of N_2O absorbed, the concentration of the N_2O gas absorbed can be calculated.

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}} \qquad (A.6)$$

Next, the Henry's constant of N_2O in Stonvent can be calculated (Equation A.7).

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}} \qquad (A.7)$$

Based on Chapter 1, the "N_2O Analogy" method is used to estimate the Henry's constant of CO_2 in Stonvent.

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}. \qquad (A.8)$$

The Henry's constant for N_2O in water is obtained from the experiment following the above calculations, replacing the subscript 'Stonvent' to 'Water'.

Meanwhile, Table A.1 shows the data for the Henry's constant of CO_2 gas in water obtained from Al-Ghawas et al. (1989).

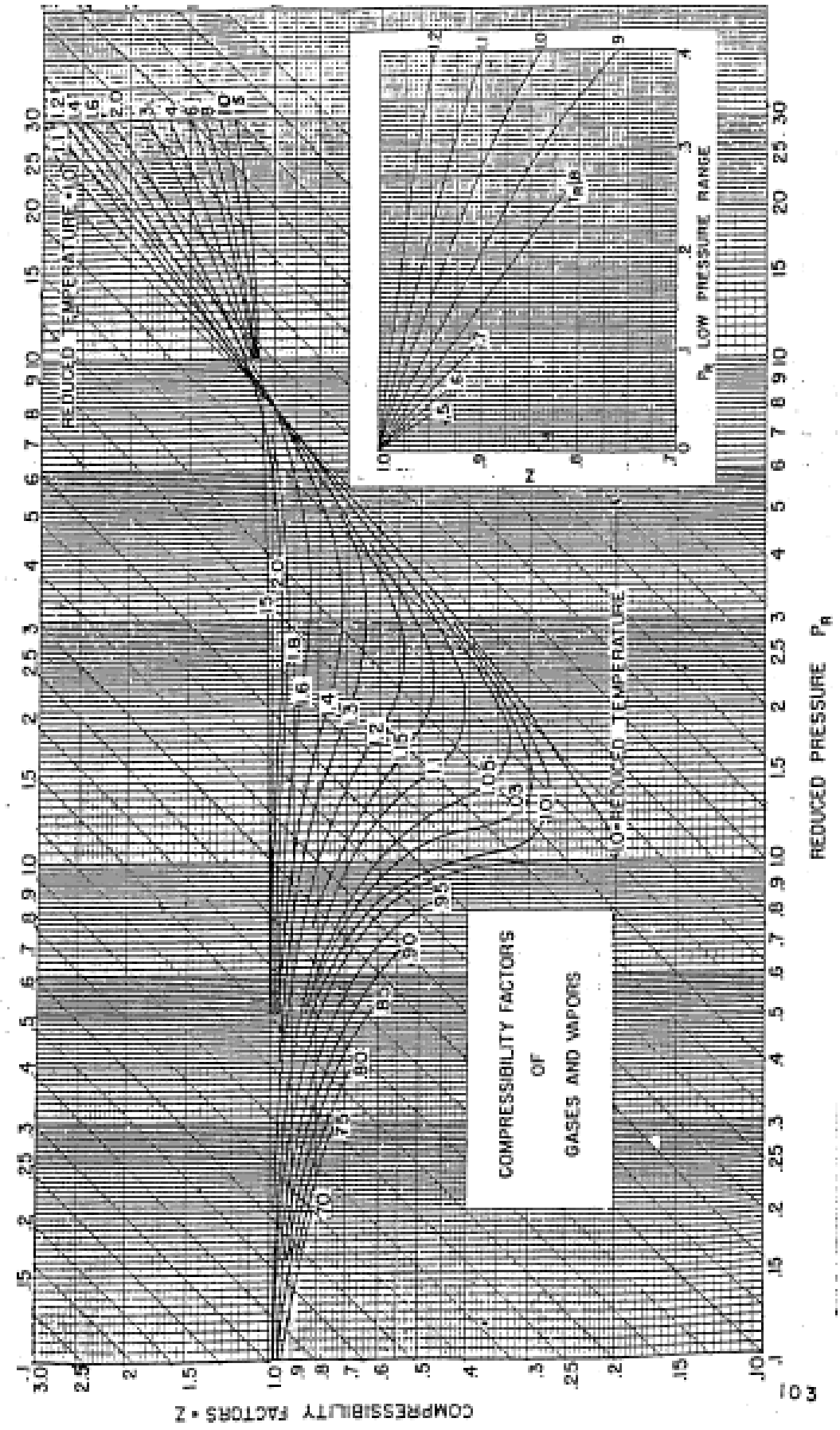

Figure A.1: Compressibility Factors Chart

Table A.1: Henry's Constant of CO_2 Gas in Water

T (K)	H (kPa.m^3/kmol)
303.15	3394.388
313.15	4249.571
323.15	5166.562

Then, the Henry's constant, H versus inverse of temperature, 1000/T is plotted for all temperatures and pressures.

1.1 Calculations Steps

1.1.1 Henry's Constant of CO_2 in Stonvent at 303.15 K and 10 bar

C. Henry's Constant for N_2O in Water at 303.15 K and 10 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{10\ \text{bar}}{72.7\ \text{bar}}$$
$$= 0.1376$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{303.15\ \text{K}}{310.15\ \text{K}}$$
$$= 0.9774$$

From the compressibility factor chart in Figure A.1,
Z = 0.95

$$\Delta P = P_1 - P_2$$
$$= 10.07 - 9.92$$
$$= 0.15\ \text{bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.15)(3)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0188\ \text{mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\, R\, T}$$
$$= \frac{(9.39)\,(0.05-0.005)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0176\ \text{mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0188 - 0.0176$$
$$= 0.0011\ \text{mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$
$$= \frac{0.0011}{0.005}$$
$$= 0.2293\ \text{mol/L}$$

$$\left(H_{N_2O}\right)_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$

$$= \frac{9.39}{0.2293}$$
$$= 40.9549 \text{ bar.L/mol}$$
$$= 4095.4850 \text{ kPa.m}^3\text{/kmol}$$

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4095.485} = 0.8288$$

D. Henry's Constant for N_2O in Stonvent at 303.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.95.

$$\Delta P = P_1 - P_2$$
$$= 11.20 - 10.79$$
$$= 0.41 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.41)(3)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0514 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$
$$= \frac{(7.43)\,(0.05-0.005)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0140 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0514 - 0.0140$$
$$= 0.0374 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.0374}{0.005}$$
$$= 7.4809 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{7.43}{7.4809}$$
$$= 0.9932 \text{ bar.L/mol}$$
$$= 99.3191 \text{ kPa.m}^3\text{/kmol}$$

E. Henry's Constant for CO_2 in Stonvent at 303.15 K and 10 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (99.3191)\,(0.8288)$$
$$= 82.3168 \text{ kPa.m}^3\text{/kmol}$$

All of the above calculation (A, B and C) is repeated for other temperatures and pressures. Below is the tabulated data calculated based on the above steps.

1.1.2 Henry's Constant of CO_2 in Stonvent at 313.15 K and 10 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 10 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{10\ \text{bar}}{72.7\ \text{bar}}$$
$$= 0.1376$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{313.15\ \text{K}}{310.15\ \text{K}}$$
$$= 1.0097$$

From the compressibility factor chart in Figure A.1,
Z = 0.955

$$\Delta P = P_1 - P_2$$
$$= 10.84 - 10.68$$
$$= 0.16\ \text{bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.16)(3)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0193\ \text{mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\, R\, T}$$
$$= \frac{(10.13)\,(0.05-0.005)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0183\ \text{mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0193 - 0.0183$$
$$= 0.0010\ \text{mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$
$$= \frac{0.0010}{0.005}$$
$$= 0.1943\ \text{mol/L}$$

$$\left(H_{N_2O}\right)_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{10.13}{0.1943}$$
$$= 52.1494\ \text{bar.L/mol}$$
$$= 5214.936\ \text{kPa.m}^3\text{/kmol}$$

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5214.936} = 0.8149$$

B. Henry's Constant for N_2O in Stonvent at 313.15 K and 10 bar

As the parameters are still the same with the above calculation,

the compressibility factor chart is Z = 0.955.

$$\Delta P = P_1 - P_2$$
$$= 10.46 - 10.09$$
$$= 0.37 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P \, V_{MV}}{Z \, R \, T}$$
$$= \frac{(0.37)(3)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0446 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm} \, (V_{EC} - V_{Stonvent})}{Z \, R \, T}$$
$$= \frac{(9.83) \, (0.05 - 0.005)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0178 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0446 - 0.0178$$
$$= 0.0269 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.0269}{0.005}$$
$$= 5.3702 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{9.83}{5.3702}$$
$$= 1.8305 \text{ bar.L/mol}$$
$$= 183.0465 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 313.15 K and 10 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (183.0465) \, (0.8149)$$
$$= 149.1617 \text{ kPa.m}^3\text{/kmol}$$

1.1.3 Henry's Constant of CO_2 in Stonvent at 323.15 K and 10 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 10 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{10 \text{ bar}}{72.7 \text{ bar}}$$
$$= 0.1376$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{323.15 \text{ K}}{310.15 \text{ K}}$$
$$= 1.0420$$

From the compressibility factor chart in Figure A.1,
Z = 0.960

$$\Delta P = P_1 - P_2$$
$$= 10.45 - 10.29$$
$$= 0.16 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.16)(3)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0186 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\, R\, T}$$
$$= \frac{(10.16)\,(0.05-0.005)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0177 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0186 - 0.0177$$
$$= 0.0009 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$
$$= \frac{0.0009}{0.005}$$
$$= 0.1768 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{10.16}{0.1768}$$
$$= 57.4692 \text{ bar.L/mol}$$
$$= 5746.9200 \text{ kPa.m}^3\text{/kmol}$$

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{5746.9200} = 0.8990$$

B. Henry's Constant for N_2O in Stonvent at 323.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.96.

$$\Delta P = P_1 - P_2$$
$$= 10.07 - 9.81$$
$$= 0.26 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.26)(3)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0302 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$

$$= \frac{(7.99)\,(0.05-0.005)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0139 \text{ mol}$$

$$n^{l}_{N_2O} = n_{N_2O} - n^{g}_{N_2O}$$
$$= 0.0302 - 0.0139$$
$$= 0.0163 \text{ mol}$$

$$C_{N_2O} = \frac{n^{l}_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.0163}{0.005}$$
$$= 3.2602 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{7.99}{3.2602}$$
$$= 2.4508 \text{ bar.L/mol}$$
$$= 245.0805 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 323.15 K and 10 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (245.0805)\,(0.8990)$$
$$= 220.3308 \text{ kPa.m}^3\text{/kmol}$$

1.1.4 Henry's Constant of CO_2 in Stonvent at 303.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 303.15 K and 45 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{45 \text{ bar}}{72.7 \text{ bar}}$$
$$= 0.6190$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{303.15 \text{ K}}{310.15 \text{ K}}$$
$$= 0.9774$$

From the compressibility factor chart in Figure A.1,
Z = 0.70

From 1.1.1, at 303.15 K,

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4095.485} = 0.8288$$

B. Henry's Constant for N_2O in Stonvent at 303.15 K and 45 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.95.

$$\Delta P = P_1 - P_2$$
$$= 45.83 - 44.21$$
$$= 1.62 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P \, V_{MV}}{Z \, R \, T}$$
$$= \frac{(1.62)(3)}{(0.7)(0.08314)(303.15)}$$
$$= 0.2755 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm} \, (V_{EC} - V_{Stonvent})}{Z \, R \, T}$$
$$= \frac{(32.62) \, (0.05 - 0.005)}{(0.7)(0.08314)(303.15)}$$
$$= 0.0832 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.2755 - 0.0832$$
$$= 0.1923 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.1923}{0.005}$$
$$= 38.4514 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{32.62}{38.4514}$$
$$= 0.8483 \text{ bar.L/mol}$$
$$= 84.8344 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 303.15 K and 45 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (84.8344) \, (0.8288)$$
$$= 70.3118 \text{ kPa.m}^3\text{/kmol}$$

1.1.5 Henry's Constant of CO_2 in Stonvent at 313.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 45 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{45 \text{ bar}}{72.7 \text{ bar}}$$
$$= 0.6190$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{313.15 \text{ K}}{310.15 \text{ K}}$$
$$= 1.0097$$

From the compressibility factor chart in Figure A.1,
Z = 0.71

From 1.1.2, at 313.15 K,

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5214.936} = 0.8149$$

B. Henry's Constant for N_2O in Stonvent at 313.15 K and 45 bar

As the parameters are still the same with the above calculation, the compressibility factor chart is Z = 0.71.

$$\Delta P = P_1 - P_2$$
$$= 44.71 - 43.29$$
$$= 1.42 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(1.42)(3)}{(0.71)(0.08314)(313.15)}$$
$$= 0.2304 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$
$$= \frac{(38.73)\,(0.05-0.005)}{(0.71)(0.08314)(313.15)}$$
$$= 0.0943 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.2304 - 0.0943$$
$$= 0.1362 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.1362}{0.005}$$
$$= 27.2331 \text{ mol/L}$$

$$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{38.73}{27.2331}$$
$$= 1.4222 \text{ bar.L/mol}$$
$$= 142.2165 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 313.15 K and 45 bar

$$(H_{CO_2})_{Stonvent} = (H_{N_2O})_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (142.2165)\,(0.8149)$$
$$= 115.8900 \text{ kPa.m}^3\text{/kmol}$$

1.1.6 Henry's Constant of CO_2 in Stonvent at 323.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 45 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{45 \text{ bar}}{72.7 \text{ bar}}$$
$$= 0.6190$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{323.15\ K}{310.15\ K}$$
$$= 1.0420$$

From the compressibility factor chart in Figure A.1,
Z = 0.7800

From 1.1.3, at 323.15 K,
$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{5746.9200} = 0.8990$$

B. Henry's Constant for N_2O in Stonvent at 323.15 K and 45 bar

As the parameters are still the same with the above calculation, the compressibility factor chart is Z = 0.78.

$$\Delta P = P_1 - P_2$$
$$= 46.56 - 45.52$$
$$= 1.04 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(1.04)(3)}{(0.78)(0.08314)(323.15)}$$
$$= 0.1489 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$
$$= \frac{(20.31)\,(0.100 - 0.005)}{(0.78)(0.08314)(323.15)}$$
$$= 0.0921 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.1489 - 0.0921$$
$$= 0.0568 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.0568}{0.005}$$
$$= 11.3618 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{20.31}{11.3618}$$
$$= 1.7876 \text{ bar.L/mol}$$
$$= 178.7566 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 323.15 K and 45 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (178.7566)\ (0.8990)$$
$$= 160.7046 \text{ kPa.m}^3\text{/kmol}$$

1.1.7 Henry's Constant of CO_2 in Stonvent at 303.15 K and 80 bar

A. Henry's Constant for N_2O in Water at 303.15 K and 80 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{80\ \text{bar}}{72.7\ \text{bar}}$$
$$= 1.1004$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{303.15\ \text{K}}{310.15\ \text{K}}$$
$$= 0.9774$$

From the compressibility factor chart in Figure A.1,
Z = 0.59

From 1.1.1, at 303.15 K,
$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{\text{water}} = \frac{3394.388}{4095.485} = 0.8288$$

B. Henry's Constant for N_2O in Stonvent at 303.15 K and 80 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.59.

$$\Delta P = P_1 - P_2$$
$$= 74.42 - 71.98$$
$$= 2.44\ \text{bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(2.44)(3)}{(0.95)(0.08314)(303.15)}$$
$$= 0.4922\ \text{mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$
$$= \frac{(31.31)\,(0.100-0.005)}{(0.95)(0.08314)(303.15)}$$
$$= 0.2000\ \text{mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.4922 - 0.2000$$
$$= 0.2922\ \text{mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.2922}{0.005}$$
$$= 58.4432\ \text{mol/L}$$

$$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{31.31}{58.4432}$$
$$= 0.5357\ \text{bar.L/mol}$$
$$= 53.5734\ \text{kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 303.15 K and 80 bar

$$(H_{CO_2})_{Stonvent} = (H_{N_2O})_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (53.5734)\ (0.8288)$$
$$= 44.4022\ kPa.m^3/kmol$$

1.1.8 Henry's Constant of CO_2 in Stonvent at 313.15 K and 80 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 80 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{80\ bar}{72.7\ bar}$$
$$= 1.1004$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{313.15\ K}{310.15\ K}$$
$$= 1.0097$$

From the compressibility factor chart in Figure A.1,
Z = 0.30

From 1.1.2, at 313.15 K,
$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5214.936} = 0.8149$

B. Henry's Constant for N_2O in Stonvent at 313.15 K and 80 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.30.

$$\Delta P = P_1 - P_2$$
$$= 79.28 - 77.97$$
$$= 1.31\ bar$$

$$n_{N_2O} = \frac{\Delta P\ V_{MV}}{Z\ R\ T}$$
$$= \frac{(1.31)(3)}{(0.30)(0.08314)(313.15)}$$
$$= 0.5031\ mol$$

$$n^g_{N_2O} = \frac{P_{eqm}\ (V_{EC} - V_{Stonvent})}{Z\ R\ T}$$
$$= \frac{(42.96)\ (0.05-0.005)}{(0.3)(0.08314)(313.15)}$$
$$= 0.2475\ mol$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.5031 - 0.2475$$
$$= 0.2556\ mol$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.2556}{0.005}$$
$$= 51.1281\ mol/L$$

$$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{42.96}{51.1281}$$
$$= 0.8402 \text{ bar.L/mol}$$
$$= 84.0242 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 313.15 K and 80 bar

$$(H_{CO_2})_{Stonvent} = (H_{N_2O})_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (84.0242)\ (0.8149)$$
$$= 68.4700 \text{ kPa.m}^3\text{/kmol}$$

1.1.9 Henry's Constant of CO_2 in Stonvent at 323.15 K and 80 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 80 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{80 \text{ bar}}{72.7 \text{ bar}}$$
$$= 1.1004$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{323.15 \text{ K}}{310.15 \text{ K}}$$
$$= 1.0420$$

From the compressibility factor chart in Figure A.1,
Z = 0.515

From 1.1.3, at 323.15 K,
$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{5746.9200} = 0.8990$

B. Henry's Constant for N_2O in Stonvent at 323.15 K and 80 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.515.

$$\Delta P = P_1 - P_2$$
$$= 76.15 - 74.26$$
$$= 1.89 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(1.89)(3)}{(0.515)(0.08314)(323.15)}$$
$$= 0.4098 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Stonvent})}{Z\, R\, T}$$
$$= \frac{(58.43)\,(0.05-0.005)}{(0.515)(0.08314)(323.15)}$$
$$= 0.1900 \text{ mol}$$

$$n^{l}_{N_2O} = n_{N_2O} - n^{g}_{N_2O}$$
$$= 0.4098 - 0.1900$$
$$= 0.2198 \text{ mol}$$

$$C_{N_2O} = \frac{n^{l}_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.2198}{0.005}$$
$$= 43.9495 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{58.43}{43.9495}$$
$$= 1.3295 \text{ bar.L/mol}$$
$$= 132.9480 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 323.15 K and 80 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (132.9480)\ (0.8990)$$
$$= 119.5221 \text{ kPa.m}^3\text{/kmol}$$

1.2 Data Tabulation for High Pressure Experiments of Stonvent

A. Henry's Constant for N_2O in Water

Pressure = 10 bar

Reduced pressure = 0.1376

T (K)	T_r	Z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2}/H_{N2O}
303.15	0.977430	0.950	10.07	9.92	9.39	0.15	0.018793	0.017647	0.001146	0.229277	40.95485	4095.485	0.828812
313.15	1.009673	0.955	10.84	10.68	10.13	0.16	0.019304	0.018333	0.000971	0.194250	52.14936	5214.936	0.814884
323.15	1.041915	0.960	10.45	10.29	10.16	0.16	0.018610	0.017726	0.000884	0.176790	57.46920	5746.920	0.899014

B. Henry's Constant for CO_2 in Stonvent

Pressure = 10 bar

Reduced pressure = 0.1376

T (K)	T_r	Z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2} ($kPa.m^3/kmol$)
303.15	0.977430	0.950	11.20	10.79	7.43	0.41	0.051368	0.013963	0.037405	7.480941	0.993191	99.31906	82.31683
313.15	1.009673	0.955	10.46	10.09	9.83	0.37	0.044641	0.017790	0.026851	5.370221	1.830465	183.0465	149.16170
323.15	1.041915	0.960	10.07	9.81	7.99	0.26	0.030240	0.013940	0.016301	3.260153	2.450805	245.0805	220.33080

Pressure = 45 bar

Reduced pressure = 0.6190

T (K)	T_r	z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2} ($kPa.m^3/kmol$)
303.15	0.977430	0.700	45.83	44.21	32.62	1.62	0.275454	0.083197	0.192257	38.45140	0.848344	84.83437	70.31175
313.15	1.009673	0.710	44.71	43.29	38.73	1.42	0.230445	0.09428	0.136166	27.23312	1.422165	142.21650	115.89000
***323.15**	1.041915	0.780	46.56	45.52	20.31	1.04	0.148876	0.092067	0.056809	11.36182	1.787566	178.75660	160.70460

Pressure = 80 bar

Reduced pressure = 1.1004

T (K)	T_r	z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2} ($kPa.m^3/kmol$)
***303.15**	0.977430	0.590	74.42	71.98	31.31	2.44	0.492233	0.200017	0.292216	58.44324	0.535734	53.57335	44.40224
313.15	1.009673	0.300	79.28	77.97	42.96	1.31	0.503139	0.247498	0.255641	51.12814	0.840242	84.02418	68.47000
323.15	1.041915	0.515	76.15	74.26	58.43	1.89	0.409771	0.190023	0.219748	43.94952	1.329480	132.948	119.52210

2. Calculation for Atmospheric Pressure

In the experiments conducted at atmospheric pressure (3 bar), only the EC is used. Volume of EC is 100 mL.

Since the pressure is at atmospheric pressure, P_1 is the initial pressure of the Equilibrium Cell when the N_2O gas is in equilibrium.

Number of moles of N_2O in the liquid phase or absorbed by the solvent is directly measured by subtracting the initial pressure of EC, P_1 to the equilibrium pressure of EC, P_2.

$$\Delta P = P_1 - P_2 \qquad \text{(A.9)}$$

$$n^l_{N_2O} = \frac{\Delta P\,(V_{EC} - V_{Stonvent})}{Z\,R\,T} \qquad \text{(A.10)}$$

Equation A.6 to Equation A.8 is similarly used in this part of experiment. The Henry's constant, H versus inverse of temperature, 1000/T is plotted for all temperatures and pressures.

The Henry's constant for N_2O in water is obtained from the experiment following the above calculations, replacing the subscript 'Stonvent' to 'Water'.

2.1 Calculations Steps

2.1.1 Henry's Constant for CO_2 in Stonvent at 303.15 K and 3 bar

A. Henry's Constant for N_2O in Water at 303.15 K and 3 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{3\text{ bar}}{72.7\text{ bar}}$$
$$= 0.0413$$

$$T_r = \frac{T}{T_c}$$
$$= \frac{303.15\text{ K}}{310.15\text{ K}}$$
$$= 0.9774$$

From the compressibility factor chart in Figure A.1,

$z = 0.985$

$$\Delta P = P_1 - P_2$$
$$= 3.36 - 3.26$$
$$= 0.10\text{ bar}$$

$$n^l_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\,R\,T}$$
$$= \frac{(3.26)\,(0.100-0.005)}{(0.985)(0.08314)(303.15)}$$
$$= 0.00038\text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$
$$= \frac{0.00038}{0.005}$$
$$= 0.0765\text{ mol/L}$$

$$(H_{N_2O})_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{3.26}{0.0765}$$
$$= 42.5980 \text{ bar.L/mol}$$
$$= 4259.795 \text{ kPa.m}^3\text{/kmol}$$

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4259.795} = 0.7968$$

B. Henry's Constant for N_2O in Stonvent at 303.15 K and 3 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.985.

$$\Delta P = P_1 - P_2$$
$$= 3.09 - 2.96$$
$$= 0.13 \text{ bar}$$

$$n^l_{N_2O} = \frac{\Delta P\,(V_{EC} - V_{Stonvent})}{Z\,R\,T}$$
$$= \frac{(0.13)\,(0.100-0.005)}{(0.985)(0.08314)(303.15)}$$
$$= 0.00050 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.00050}{0.005}$$
$$= 0.0995 \text{ mol/L}$$

$$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{2.96}{0.0995}$$
$$= 29.7522 \text{ bar.L/mol}$$
$$= 2975.223 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 303.15 K and 3 bar

$$(H_{CO_2})_{Stonvent} = (H_{N_2O})_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (2975.223)\,(0.7968)$$
$$= 2370.785 \text{ kPa.m}^3\text{/kmol}$$

2.1.2 Henry's Constant for CO_2 in Stonvent at 313.15 K and 3 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 3 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{3 \text{ bar}}{72.7 \text{ bar}}$$
$$= 0.0413$$

$$T_r = \frac{T}{T_c}$$

$= \frac{313.15\ K}{310.15\ K}$

$= 1.0097$

From the compressibility factor chart in Figure A.1,

z = 0.987

$\Delta P = P_1 - P_2$

$= 3.36 - 3.28$

$= 0.08$ bar

$n^l_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\,R\,T}$

$= \frac{(3.06)\,(0.100-0.005)}{(0.987)(0.08314)(313.15)}$

$= 0.00030$ mol

$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$

$= \frac{0.00030}{0.005}$

$= 0.0591$ mol/L

$(H_{N_2O})_{Water} = \frac{P_{eqm}}{C_{N_2O}}$

$= \frac{3.28}{0.0612}$

$= 51.7343$ bar.L/mol

$= 5173.427$ kPa.m^3/kmol

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 4249.571.

$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5173.427} = 0.8214$

B. <u>Henry's Constant for N_2O in Stonvent at 313.15 K and 3 bar</u>

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.987.

$\Delta P = P_1 - P_2$

$= 3.55 - 3.44$

$= 0.11$ bar

$n^l_{N_2O} = \frac{\Delta P\,(V_{EC} - V_{Stonvent})}{Z\,R\,T}$

$= \frac{(0.11)\,(0.100-0.005)}{(0.987)(0.08314)(313.15)}$

$= 0.00041$ mol

$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$

$= \frac{0.00041}{0.005}$

$= 0.0813$ mol/L

$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$

$= \frac{3.44}{0.0813}$

= 42.2973 bar.L/mol
= 4229.730 kPa.m^3/kmol

C. Henry's Constant for CO_2 in Stonvent at 313.15 K and 3 bar

$$\left(H_{CO_2}\right)_{Stonvent} = \left(H_{N_2O}\right)_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
= (4229.730) (0.8214)
= 3474.396 kPa.m^3/kmol

2.1.3 Henry's Constant for CO_2 in Stonvent at 323.15 K and 3 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 3 bar

$$P_r = \frac{P}{P_c}$$
$$= \frac{3 \text{ bar}}{72.7 \text{ bar}}$$
= 0.0413

$$T_r = \frac{T}{T_c}$$
$$= \frac{323.15 \text{ K}}{310.15 \text{ K}}$$
= 1.0419

From the compressibility factor chart in Figure A.1,
z = 0.99

$$\Delta P = P_1 - P_2$$
= 3.21 – 3.14
= 0.07 bar

$$n^l_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{Water})}{Z\,R\,T}$$
$$= \frac{(3.14)\,(0.100-0.005)}{(0.99)(0.08314)(323.15)}$$
= 0.00025 mol

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Water}}$$
$$= \frac{0.00025}{0.005}$$
= 0.0500 mol/L

$$\left(H_{N_2O}\right)_{Water} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{3.14}{0.0500}$$
= 62.7984 bar.L/mol
= 6279.836 kPa.m^3/kmol

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 5166.562.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{6279.836} = 0.8227$$

B. Henry's Constant for N_2O in Stonvent at 323.15 K and 3 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.99.

$$\Delta P = P_1 - P_2$$
$$= 3.45 - 3.36$$
$$= 0.09 \text{ bar}$$

$$n^l_{N_2O} = \frac{\Delta P\,(V_{EC} - V_{Stonvent})}{Z\,R\,T}$$
$$= \frac{(0.09)\,(0.100-0.005)}{(0.99)(0.08314)(323.15)}$$
$$= 0.00032 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{Stonvent}}$$
$$= \frac{0.00032}{0.005}$$
$$= 0.0643 \text{ mol/L}$$

$$(H_{N_2O})_{Stonvent} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{3.36}{0.0643}$$
$$= 52.2653 \text{ bar.L/mol}$$
$$= 5226.530 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in Stonvent at 323.15 K and 3 bar

$$(H_{CO_2})_{Stonvent} = (H_{N_2O})_{Stonvent} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (5226.530)\,(0.8227)$$
$$= 4299.983 \text{ kPa.m}^3\text{/kmol}$$

2.2 Data Tabulation for Atmospheric Pressure Experiments

Pressure = 3 bar
Reduced pressure = 0.0413

A. Henry's Constant for N_2O in Water

T (K)	T_r	Z	P_1 (bar)	P_{eqm} (bar)	ΔP (bar)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2}/H_{N2O}
303.15	0.977430	0.985	3.36	3.26	0.10	0.00038	0.0765	42.5980	4259.795	0.7968
313.15	1.009673	0.987	3.14	3.06	0.08	0.00030	0.0591	51.7343	5173.427	0.8214
323.15	1.041915	0.990	3.21	3.14	0.07	0.00025	0.0500	62.7984	6279.836	0.8227

B. Henry's Constant for CO_2 in Stonvent

T (K)	T_r	Z	P_1 (bar)	P_{eqm} (bar)	ΔP (bar)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} ($kPa.m^3/kmol$)	H_{CO2} ($kPa.m^3/kmol$)
303.15	0.977430	0.985	3.09	2.96	0.13	0.00050	0.0995	29.7522	2975.223	2370.785
313.15	1.009673	0.987	3.55	3.44	0.11	0.00041	0.0813	42.2973	4229.73	3474.396
323.15	1.041915	0.990	3.45	3.36	0.09	0.00032	0.0643	52.2653	5226.53	4299.983

3. Calculations for CO_2 in MEA at High Pressure (10 & 45) bar

Using the new volume of EC, which is 100 mL, the Henry's constant of CO_2 in MEA at 10 and 45 bar is calculated by referring to the steps in 1.1 above. 80 bar pressure was not able to be conducted due to limited time.

3.1 Calculations Steps

3.1.1 Henry's Constant of CO_2 in MEA at 303.15 K and 10 bar

A. Henry's Constant for N_2O in Water at 303.15 K and 10 bar

From 1.1.1,
$(H_{N_2O})_{Water}$ = 4095.4850 kPa.m^3/kmol

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4095.485} = 0.8288$$

B. Henry's Constant for N_2O in MEA at 303.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.95.

$$\Delta P = P_1 - P_2$$
$$= 10.54 - 10.15$$
$$= 0.39 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.39)(3)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0489 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$
$$= \frac{(9.72)\,(0.100-0.005)}{(0.95)(0.08314)(303.15)}$$
$$= 0.0386 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0489 - 0.0386$$
$$= 0.0103 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$
$$= \frac{0.0103}{0.005}$$
$$= 2.0597 \text{ mol/L}$$

$$(H_{N_2O})_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{9.72}{7.4809}$$
$$= 4.7191 \text{ bar.L/mol}$$
$$= 471.9058 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in MEA at 303.15 K and 10 bar

$$(H_{CO_2})_{MEA} = (H_{N_2O})_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (471.9058)\ (0.8288)$$
$$= 82.3168\ \text{kPa.m}^3/\text{kmol}$$

3.1.2 Henry's Constant of CO_2 in MEA at 313.15 K and 10 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 10 bar

From 1.1.2,
$(H_{N_2O})_{Water} = 5214.936\ \text{kPa.m}^3/\text{kmol}$

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.
$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5214.936} = 0.8149$

B. Henry's Constant for N_2O in MEA at 313.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.955.

$$\Delta P = P_1 - P_2$$
$$= 10.03 - 9.68$$
$$= 0.35\ \text{bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.35)(3)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0422\ \text{mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$
$$= \frac{(9.44)\ (0.100-0.005)}{(0.955)(0.08314)(313.15)}$$
$$= 0.0361\ \text{mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0422 - 0.0361$$
$$= 0.0062\ \text{mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$
$$= \frac{0.0062}{0.005}$$
$$= 1.2323\ \text{mol/L}$$

$$(H_{N_2O})_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{9.44}{1.2323}$$
$$= 7.6607\ \text{bar.L/mol}$$
$$= 766.0726\ \text{kPa.m}^3/\text{kmol}$$

C. Henry's Constant for CO_2 in MEA at 313.15 K and 10 bar

$$\left(H_{CO_2}\right)_{MEA} = \left(H_{N_2O}\right)_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (766.0726)\ (0.8149)$$
$$= 624.260 \text{ kPa.m}^3\text{/kmol}$$

3.1.3 Henry's Constant of CO_2 in MEA at 323.15 K and 10 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 10 bar

From 1.1.3,
$\left(H_{N_2O}\right)_{Water} =$ 5746.9200 kPa.m^3/kmol

From Table A.1, the Henry's constant of CO_2 gas in water at this temperature is 3394.388.
$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{5746.9200} = 0.8990$

B. Henry's Constant for N_2O in MEA at 323.15 K and 10 bar

As the parameters are still the same with the above calculation,
the compressibility factor chart is Z = 0.96.

$$\Delta P = P_1 - P_2$$
$$= 10.25 - 9.90$$
$$= 0.35 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(0.35)(3)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0407 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$
$$= \frac{(9.61)\ (0.05 - 0.005)}{(0.96)(0.08314)(323.15)}$$
$$= 0.0354 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.0407 - 0.0354$$
$$= 0.0053 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$
$$= \frac{0.0053}{0.005}$$
$$= 1.0627 \text{ mol/L}$$

$$\left(H_{N_2O}\right)_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{9.61}{1.0627}$$
$$= 9.0432 \text{ bar.L/mol}$$

= 904.3169 kPa.m^3/kmol

C. Henry's Constant for CO_2 in MEA at 323.15 K and 10 bar

$$(H_{CO_2})_{MEA} = (H_{N_2O})_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$

= (904.3169) (0.8990)

= 812.9936 kPa.m^3/kmol

3.1.4 Henry's Constant of CO_2 in MEA at 303.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 303.15 K and 45 bar

From 1.1.1,

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{3394.388}{4095.485} = 0.8288$$

B. Henry's Constant for N_2O in MEA at 303.15 K and 45 bar

As the parameters are still the same with the above calculation, the compressibility factor chart is Z = 0.70.

$$\Delta P = P_1 - P_2$$

= 45.04 – 43.32

= 1.72 bar

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$

$$= \frac{(1.72)(3)}{(0.7)(0.08314)(303.15)}$$

= 0.2925 mol

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$

$$= \frac{(43.12)\,(0.100-0.005)}{(0.7)(0.08314)(303.15)}$$

= 0.2322 mol

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$

= 0. 2925 – 0.2322

= 0.0603 mol

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$

$$= \frac{0.0603}{0.005}$$

= 12.0565 mol/L

$$(H_{N_2O})_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$

$$= \frac{43.12}{12.0565}$$

= 3.5765 bar.L/mol

= 357.649 kPa.m^3/kmol

C. Henry's Constant for CO_2 in MEA at 303.15 K and 45 bar

$$(H_{CO_2})_{MEA} = (H_{N_2O})_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (357.649)\ (0.8288)$$
$$= 296.4237 \text{ kPa.m}^3\text{/kmol}$$

3.1.5 Henry's Constant of CO_2 in MEA at 313.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 313.15 K and 45 bar

From 1.1.2, at 313.15 K,

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{4249.571}{5214.936} = 0.8149$$

B. Henry's Constant for N_2O in MEA at 313.15 K and 45 bar

As the parameters are still the same with the above calculation, the compressibility factor chart is Z = 0.71.

$$\Delta P = P_1 - P_2$$
$$= 45.09 - 43.53$$
$$= 1.56 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(1.56)(3)}{(0.71)(0.08314)(313.15)}$$
$$= 0.2532 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$
$$= \frac{(43.02)\ (0.100 - 0.005)}{(0.71)(0.08314)(313.15)}$$
$$= 0.2211 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.2532 - 0.2211$$
$$= 0.0321 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$
$$= \frac{0.0321}{0.005}$$
$$= 6.4168 \text{ mol/L}$$

$$(H_{N_2O})_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{43.02}{6.4168}$$
$$= 6.7043 \text{ bar.L/mol}$$
$$= 670.4311 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in MEA at 313.15 K and 45 bar

$$(H_{CO_2})_{MEA} = (H_{N_2O})_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (670.4311)\ (0.8149)$$
$$= 546.3236 \text{ kPa.m}^3\text{/kmol}$$

3.1.6 Henry's Constant of CO_2 in MEA at 323.15 K and 45 bar

A. Henry's Constant for N_2O in Water at 323.15 K and 45 bar

From 1.1.3, at 323.15 K,

$$\left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water} = \frac{5166.562}{5746.9200} = 0.8990$$

B. Henry's Constant for N_2O in MEA at 323.15 K and 45 bar

As the parameters are still the same with the above calculation, the compressibility factor chart is Z = 0.78.

$$\Delta P = P_1 - P_2$$
$$= 44.94 - 43.41$$
$$= 1.53 \text{ bar}$$

$$n_{N_2O} = \frac{\Delta P\, V_{MV}}{Z\, R\, T}$$
$$= \frac{(1.53)(3)}{(0.78)(0.08314)(323.15)}$$
$$= 0.2190 \text{ mol}$$

$$n^g_{N_2O} = \frac{P_{eqm}\,(V_{EC} - V_{MEA})}{Z\, R\, T}$$
$$= \frac{(42.87)\,(0.100-0.005)}{(0.78)(0.08314)(323.15)}$$
$$= 0.1943 \text{ mol}$$

$$n^l_{N_2O} = n_{N_2O} - n^g_{N_2O}$$
$$= 0.2190 - 0.1943$$
$$= 0.0247 \text{ mol}$$

$$C_{N_2O} = \frac{n^l_{N_2O}}{V_{MEA}}$$
$$= \frac{0.0247}{0.005}$$
$$= 4.9372 \text{ mol/L}$$

$$(H_{N_2O})_{MEA} = \frac{P_{eqm}}{C_{N_2O}}$$
$$= \frac{42.87}{4.9372}$$
$$= 8.6830 \text{ bar.L/mol}$$
$$= 868.2978 \text{ kPa.m}^3\text{/kmol}$$

C. Henry's Constant for CO_2 in MEA at 323.15 K and 45 bar

$$(H_{CO_2})_{MEA} = (H_{N_2O})_{MEA} \left(\frac{H_{CO_2}}{H_{N_2O}}\right)_{water}$$
$$= (868.2978)\ (0.8990)$$
$$= 780.6119 \text{ kPa.m}^3\text{/kmol}$$

3.2 Data Tabulation for High Pressure Experiments of MEA

Henry's Constant for CO_2 in MEA

Pressure = 10 bar
Reduced pressure = 0.1376

T (K)	T_r	Z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} (kPa.m^3/kmol)	H_{CO2} (kPa.m^3/kmol)
303.15	0.977430	0.950	10.54	10.15	9.72	0.39	0.048862	0.038564	0.010299	2.059733	4.719058	471.9058	391.1212
313.15	1.009673	0.955	10.03	9.68	9.44	0.35	0.042228	0.036067	0.006161	1.232259	7.660726	766.0726	624.2603
323.15	1.041915	0.960	10.25	9.90	9.61	0.35	0.040708	0.035395	0.005313	1.062681	9.043169	904.3169	812.9936

Pressure = 45 bar
Reduced pressure = 0.6190

T (K)	T_r	z	P_1 (bar)	P_2 (bar)	P_{eqm} (bar)	ΔP (bar)	n_{N2O} (mol)	$n_{N2O\ (g)}$ (mol)	$n_{N2O\ (l)}$ (mol)	C_{N2O} (mol/L)	H_{N2O} (bar.L/mol)	H_{N2O} (kPa.m^3/kmol)	H_{CO2} (kPa.m^3/kmol)
303.15	0.977430	0.700	45.04	43.32	43.12	1.72	0.292458	0.232175	0.060283	12.05652	3.576490	357.6490	296.4237
313.15	1.009673	0.710	45.09	43.53	43.02	1.56	0.253165	0.221081	0.032084	6.416767	6.704311	670.4311	546.3236
323.15	1.041915	0.780	44.94	43.41	42.87	1.53	0.219020	0.194333	0.024686	4.937246	8.682978	868.2978	780.6119